ABANDONED GOLD MINE TAILINGS: MINERALOGY, ENVIRONMENTAL HAZARDS, VALORIZATION, AND REMEDIATION STRATEGIES – A MULTIDISCIPLINARY APPROACH.

BY

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ARTICLES PUBLISHED OR WRITTEN FOR PUBLICATION

Journal Papers

* Uchenna Okereafor, Elizabeth Makhatha, Lukhanyo Mekuto, Vuyo Mavumengwana, ***Dataset on assessment of pollution level of selected trace metals in farming area within the proximity of a gold mine dump, Ekuhurleni, South Africa,*** Data in brief, 26:10447326. https://doi.org/10.1016/j.dib.2019.104473.

* Uchenna Okereafor, Elizabeth Makhatha, Lukhanyo Mekuto, Nkemdinma Uche-Okereafor, Tendani Sebola, Vuyo Mavumengwana, ***Toxic metal Implications on Agricultural Soils, Plants, Animals, Aquatic Life and Human Health – A Review.*** International Journal of Environmental Research and Public Health, 17 (7):2204. https://doi.org/10.3390/ijerph17072204.

* Uchenna Okereafor, Elizabeth Makhatha, Lukhanyo Mekuto, Vuyo Mavumengwana, ***Gold mine tailings – potential source of silica sand for glassmaking industries.*** Minerals 2020, 10, 448; doi:10.3390/min10050448.

Book Chapters

* Uchenna Okereafor, Elizabeth Makhatha, Lukhanyo Mekuto, Vuyo Mavumengwana, ***Evaluation of trace elemental levels as pollution indicators in an abandoned gold mine dump in Ekuhurleni area, South Africa. In: Trace elements in the environment – New approaches and recent advances, Editor: Dr. Mario Alfonso Murillo-Tovar,*** IntechOpen, submitted: June 12th, 2019, reviewed: September 6th, 2019, published: October 22nd, 2019. DOI: 10.5772/intechopen.89582.

* Uchenna Okereafor, Elizabeth Makhatha, Lukhanyo Mekuto, Vuyo Mavumengwana, ***Mobility of trace element contaminants from abandoned gold mine dump to stream waters in an Agricultural active area. In: Trace elements in the environment – New approaches and recent advances, Editor: Dr. Mario Alfonso Murillo-Tovar,*** IntechOpen, submitted: June 12th, 2019, reviewed: December 10th, 2019, published: February 11th, 2020. DOI: 10.5772/intechopen.90818.

Conference Papers

* Okereafor GU, Makhatha E, Hassina M, Mavumengwana V, ***Assessment of the impacts of mine tailings from a South African gold mine: an example from Blesbokspruit Conservation Trust, Springs, Ekurhuleni,*** General Assembly 2018, European Geosciences Union, Vienna, Austria.

* Okereafor GU, Makhatha E, Mekoto L, Mavumengwana V, ***The impact of mining activity on the surrounding soils near a gold mine in Blesbokspruit - Ekurhuleni South African***, 130th Geological Society of America International Conference, 4 – 7 November 2018, Indianapolis, Indiana, USA.

* Okereafor GU, Makhatha E, Mekoto L, Mavumengwana V, ***Mobility of contaminants from abandoned gold mine dumps to stream waters in an agricultural activity area***, 130th Geological Society of America International Conference, 4 – 7 November 2018, Indianapolis, Indiana, USA.

* Okereafor GU, Makhatha E, Mekoto L, Mavumengwana V, ***Assessing the effectiveness of Hyparrhenia hirta in the rehabilitation of the ecosystem of a gold mine dump***, 7th International Conference on Environment Pollution and Prevention (ICEPP), 18 – 20 December 2019, Melbourne, Australia.

* Okereafor GU, Makhatha E, Mekoto L, Mavumengwana V, ***Abandoned gold mine tailings: an alternative raw material for South Africa's glass industry***, 35th International Conference on Solid Waste Technology and Management, 22 – 25 March 2020, Annapolis (Washington, D.C.) U.S.A.

* Okereafor GU, Mekoto L, ***Assessment of Metal Content of Waste laptop computers and Estimation of Their Recovery Potential in Randburg Central Business District of Johannesburg, South Africa.***, 35th International Conference on Solid Waste Technology and Management, 22 – 25 March 2020, Annapolis (Washington, D.C.) U.S.A.

EXECUTIVE SUMMARY

In general, the role of mining cannot be overemphasized. Many nations have not gone bankrupt because of the support received from mining outputs in terms of revenue from the exportation of minerals. Exploration activities have continued to create both formal and informal job opportunities, energy, raw materials for industries, and the development of towns. It is no doubt that mining plays a crucial role in the socio-economic well-being of a nation. South Africa owing to her large mineral deposits, has remained very active and a key contributor to the global demand of various minerals such as gold, diamond, iron, zinc, etc. which has resulted in mining operations at virtually every corner of the country. Regrettably, these mining activities do not come cheap as they leave some negative footprints in the form of waste materials known as tailings which impact the environment, humans, plants, and animals. Few reports on the characterisation of these tailings are available but none had considered their potential as raw material in applications such as the manufacture of glass which requires more silica material.

Characterisation plays a vital role in the study of mine wastes such as tailings, as it provides useful information about the safety of its disposal into the environment. The composition of such complex waste material had been based solely on characterisation, which stirs discussions around safety and environmental health. It was therefore imperative to consider other studies besides the characterisation of mine tailings to better understand some of the intricacies it poses to the ecosystem.

The first phase of the study considered the physicochemical characterisation of gold mine tailings located in proximity to a wetland in the mining community of Blesbokspruit in Ekuhurleni Metropolitan area of Gauteng Province. Using 5 g of 20 representative soil samples, the prevalence of selected elements was determined. The soils recorded very strongly acidic values ranging from 3.86 to 4.34 linked with a low cation exchange capacity (CEC). The elemental composition of the tailings materials on the bases of X-ray fluorescence (XRF) analysis revealed average values of trace element oxides such as Na_2O (0.18 %), MgO (0.63 %), Al_2O_3 (6.51 %), SiO_2 (81.83 %), P_2O_5 (0.04 %), SO_3 (3.40 %), K_2O (1.98 %), CaO (0.45 %), TiO_2 (0.51 %), Cr_2O_3 (0.17 %), MnO (0.04 %), Fe_2O_3 (3.59 %), NiO (0.04 %), As_2O_3 (0.02 %), with Rb_2O and SrO falling below 0.01 %.

With the aid of pollution indices such as contamination factor, degree of contamination, geo-accumulation index, pollution load index and the United States Environmental Protection Agency benchmarks for toxic metals concentration in soil, Trace metals (TM) contamination levels were evaluated. The average concentration of various trace metals were [Cr] 861.5 mg/kg; [Al] 326.8 mg/kg; [As] 202.2 mg/kg; [Fe] 134.3 mg/kg; [Pb] 123.7 mg/kg; [Co] 28.8 mg/kg; [Ni] 25.4 mg/kg; [Ti] 8.5 mg/kg; [Cd] 8.3 mg/kg; [Zn] 4.5 mg/kg, and [Cu] 0.2 mg/kg. A very high degree of contamination and a polluted status were observed on account of the average contamination factor and polluted load index of the trace metals respectively

In a subsequent study, the mobility of trace element contaminants from abandoned gold mine dump to stream waters in an agricultural active area was evaluated. It was revealed that the tailing sediments were largely comprised of fine sands that are loosely packed and prone to erosion thus supporting the migration of trace metal contaminants. The ability of plants to survive in the area based on the recorded physiochemical data such as acidity and electrical conductivity of the tailing sediments, and water from wetland is compromised. A continuous erosion of sediments from the tailing dump site into the wetland and streams increases the migration of Al, As, Pb and Cr, which were observed to be in elevated concentrations. Thus, endangering sustainable agricultural activities within the surrounding farmlands as water sources were prone to contamination from potentially toxic metals trapped in tailing sediments especially given their high concentrations. The dispersion of such tailing sediments not only affects the agricultural activities within the studied area but may also have a health-related effect on the human population that reside in proximity to this mine dump.

As a remediation strategy, indigenous plant species was assessed for metal uptake. The study revealed that the grass - *Hyparrhenia hirta* contained toxic metals mean concentrations, mg/kg, (Cu [46.10], Zn [40.08], Pb [859.12], Cr [618.26], Co [151.70], Ni [2308.41]) with alarming pH range of 5.13 – 5.33 that poses danger to the environment. *Hyparrhenia hirta* found within the tailings dump may be qualified as an hyperaccumulator as it is suitable for rehabilitation of the tailings dump. However, the usage of *Hyparrhenia hirta* for the revegetation of the site may not be efficient due to the sparsely growth pattern observed leaving the area susceptible to soil erosion after toxic rainfall or windstorm, thus transporting tailings to nearby water sources.

In the industrial manufacture of glass, silica is a major component. This study therefore evaluated the quantity of silica in the gold mine tailings and observed an average composition of 88.72 %. Batch compositions of 50 g with averages of 10.00 mass % of $CaCO_3$, 5.0 mass% of Na_2CO_3, and 35.00 mass% of SiO_2 at temperatures of between 1500 ºC and 1600 ºC respectively, resulted in the production of a green coloured glass.

In conclusion, our findings validate various uncertainties on the implications of mine tailings to the environment, agricultural activities and human health. The mining process employed, and target mineral affects the physiological and mineralogical contents of the tailings. The poor management of tailings facilities results in release of toxic elements into surrounding soils, water, and the atmosphere. As much as governments around the world claim that technological innovations and applications in the mining industry has eliminated the problems associated with mining, continued exposure to tailings dump of several decades have negative effects on the ecosystem due to the presence and release of potentially trace metals. Nevertheless, as a proactive measure in safeguarding our environment, gold mine tailings could be used as cheap sources of silica sand required for the manufacture of glass. The value-added product not only provide additional income to the mining industries but will also serve as business/employment opportunities for millions of residents within these mine tailings dumps.

Key words: Contamination, mining, tailings dump, trace metals, environment.

LAYOUT OF THESIS

This thesis covers studies on Abandoned Gold mine tailings: mineralogy, environmental hazards, valorization, and remediation strategies – A multidisciplinary approach. A brief outline of the chapters presented in this thesis is provided below.

Chapter One: General introduction.

This chapter provides a general overview of the research study, providing relevant background information as well as describing the problem under investigation. The chapter also highlights the assumptions (hypothesis), aim and objectives of the study.

Chapter Two: Literature review.

This chapter presents an in-depth evaluation of the research focus. It describes mining processes carried out in the quest for specific mineral, to the generation of wastes which serves as sources of toxic metal, waste treatment, disposal, and management as well as the resultant implications of such wastes to the ecosystem (air, soil, water, plants, humans, and animals).

This aspect of the thesis titled '*Toxic Metal Implications on Agricultural Soils, Plants, Animals, Aquatic life and Human Health: A review.'* has been published in the journal - *International Journal of Environmental Research and Public Health 17(7), 2204.* *https://doi.org/10.3390/ijerph17072204*.

Chapter Three: Evaluation of trace elemental levels as pollution indicators in an abandoned gold mine dump in Ekuhurleni area, South Africa.

Chapter Three describes the contamination level of identified trace metals in an abandoned mine tailing dump over time using techniques such as XRF, and ICP-OES. Also applied were various pollution indices such as contamination factor, degree of contamination, geo-accumulation index, pollution load index and the United States Environmental Protection Agency benchmarks for toxic metals concentration in soil. The work described in this chapter has been published as a book chapter in the journal *IntechOpen* with the title "*Evaluation of trace elemental levels as pollution indicators in an abandoned gold mine dump in Ekuhurleni area, South Africa. In: Trace elements* *in the environment – New approaches and recent advances*, Editor: Dr. Mario Alfonso Murillo-Tovar, submitted: June 12th, 2019, reviewed: September 6th, 2019, published: October 22nd, 2019. DOI: 10.5772/intechopen.89582.

Chapter Four: Mobility of trace element contaminants from abandoned gold mine dump to stream waters in an agricultural active area.

Chapter Four describes the assessment of the general quality of water being utilized for irrigation purposes and feeding of farm animals using procedural methods in a bid to identify relations between tailings and stream water contamination. The work described in this chapter has been accepted for publication as a book chapter in the journal *IntechOpen* with the title "*Mobility of trace element contaminants from abandoned gold mine dump to stream waters in an agricultural active area. In: Trace elements in the environment – New approaches and recent advances*, Editor: Dr. Mario Alfonso Murillo-Tovar, submitted: June 12th, 2019, reviewed: December 10th, 2019, published: February 11th, 2020. DOI: 10.5772/intechopen.90818.

Chapter Five: Assessing the effectiveness of *Hyparrhenia hirta* in the rehabilitation of the ecosystem of a gold mine dump.

Chapter Five focused on the assessment of toxic metal contents of the gold tailings sediments at the same time analyzing the uptake of such toxic metals by *Hyparrhenia hirta* an indigenous grass specie. This section of the thesis was presented at the *7th International Conference on Environment Pollution and Prevention (ICEPP)*, 18 – 20 December 2019, Melbourne, Australia and has been published online with E3S Web of Conferences (Open Access proceedings in Environment, Energy and Earth Sciences).
https://www.e3s-conferences.org/articles/e3sconf/abs/2020/18/contents/contents.html.

Chapter Six: Gold mine tailings: A potential source of silica sand for glassmaking industries.

Considering that often, mining wastes such as tailings are left unattended to with no clue of what to do with the sediments that occupy vast land area that could be used for other socioeconomic ventures, this chapter highlights on the prospect of utilizing tailings from an abandoned gold mine dump as raw materials in the production of glass. This section of the thesis was accepted for presentation at the *35th International Conference on Solid Waste Technology and Management*, 22 – 25 March 2020, Annapolis (Washington, D.C.) U.S.A. The conference was cancelled unfortunately due to restriction on International travels as a precautionary measure in dealing with the global issue of Corona Virus (COVID-19). This led to a further review and subsequent submission of this aspect of the study with a new title "Gold mine tailings – potential source of silica sand for glassmaking industries" for consideration for publication in the journal – Minerals.

Chapter Seven: General discussion and conclusion.

This chapter reiterates the research focus (problem statement and aim) of this thesis as well as presents an overall discussion of the issues addressed in Chapters Three, Four, Five, and Six and reaches a final judgment. Recommendations and prospects for future studies are also provided.

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LIST OF ABBREVIATIONS

Ag	Silver
Al	Aluminium
AMD	Acid Mine Drainages
ARDS	Adult Respiratory Distress Syndrome
As	Arsenic
ATP	Adenosine triphosphate
ATSMC	Agency for Toxic Substances Management Committee
BAC	Biological Accumulating Coefficient
BGMC	British Glass Manufacturers Confederation
BS	British Standard
Ca	Calcium
Ca^+	Calcium ion
CAPD	Central Auditory Processing Disorder
CCME	Canadian Council of Ministers of the Environment
CD	Contamination Degree
Cd	Cadmium
CEC	Cation Exchange Capacity
CF	Contamination Factor
Co	Cobalt

CO_2	Carbon dioxide
Cr	Chromium
CTBs	Chemical Time Bombs
Cu	Copper
DNA	Deoxyribonucleic Acid
EC	Electrical Conductivity
EDX	Energy Dispersive X-ray
Eh	Redox Potential
EMCB	Environmental Mining Council of British Columbia
Fe	Iron
H	Hydrogen
HB	Heidelburg
HCl	Hydrochloric Acid
Hg	Mercury
Hg^{2+}	Mercury ion
HgS	Mercury sulfide
H_2O_2	Hydrogen peroxide
I	Iodine
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectrometry
IQ	Intelligence Quotient
ISQG	Interim Sediment Quality Guidelines

K	Potassium
LOI	Loss of Ignition
Mg	Magnesium
Mn	Manganese
MT	Mine Tailings
N	Nitrogen
Na	Sodium
Na^+	Sodium ion
Ni	Nickel
O	Oxygen
OH	Hydroxyl
OM	Organic matter
P	Phosphorus
Pb	Lead
PLI	Pollution Load Index
PVC	Polyvinyl chloride
ROM	Run of Mine
ROS	Reactive Oxygen Species
SB	Suikerbosrand
Sb	Antimony
Se	Selenium

SEM	Scanning Electron Microscope
Si	Silicon
TD	Tailings Dam
TDS	Total Dissolved Solids
Ti	Titanium
Tl	Thallium
TM	Trace Metal
U	Uranium
USA	United States of America
USEPA	United States Environmental Protection Agency
V	Vanadium
WHO	World Health Organisation
WL	Wetland
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
Zn	Zinc

LIST OF SYMBOLS AND UNITS

À	Angstrom
%	Percentage
±	Plus, or minus
<	Less than
>	Greater than
cm	Centimeter
°C	Degree Celsius
°F	Degree Fahrenheit
µg	Microgram
µg/mL	Microgram per milliliter
µm	Micrometer
µs/cm	Microsecond per centimeter
g	Gram(s)
g/L	Gram(s) per litre
kg	Kilogram
kV	Kilovolts
nm	Nanometer
mg/kg	Milligram per kilogram
mg/L	Milligram per litre
M	Mole
Min	Minute(s)
Ml	Microliter
mA	Milliampere
mL	Millilitre
mm	Millimeter
ppm	Parts per million
Sec	Second(s)
v/v	Volume by volume

CHAPTER 1

GENERAL INTRODUCTION

General Introduction

1.1 Background.

Several years and continued mining activities in South Africa have resulted in a national crisis as reported by mining specialists, media houses and various stakeholders. Air and water pollution emanating from mining, toxic wastes, acid mine drainages (AMD) and abandoned mines remain potential dangers to the living conditions of South Africans, their communities, and the environment at large (Capel, 2012). The environment suffers the single most destructive impact of mining.

A major contributor to the alarming level of pollution in South Africa is mining waste. Being a country with limited water sources, gold and platinium mines, old coal fields amongst others are aiding the contamination on both ground and surface water which is reportedly at an epic state due to trace metal seepages (Ochieng *et al*., 2010; McCarthy, 2011). This trend poses a threat to the well-being of the wider populace. Deleterious health implications linked to water contamination and specific trace metals from mine wastes are at alarming levels globally (Ebenebe *et al*., 2017). As such, there have been several health complications with people within the proximity of mine tailings dumps. This has thus become a public health problem hence calls for the reclamation of tailings dumps. Nature has always been a reservoir of very useful and important minerals but has somehow been overlooked in recent times. Owing to the current climate change, it is important to investigate many of the mine tailings dumps of several decades to ascertain their current composition and safety.

It is therefore pertinent to scientifically focus on the short and long-term impact of contaminated seepages released from tailings dumps of the gold mining industry, dust generation, and surface run-off.

1.2 Rationale.

In South Africa, the mining of minerals such as gold, copper, platinum, etc. have been sources of economic boost through revenue generation. However, the extraction processes have resulted in vast volumes of waste material, mainly in the form of tailings materials. Inconsistency in government policies and legislations coupled with inadequate management of most of the tailings dumps lead to environmental calamities such as the occurrence of acid mine drainage (AMD), soil degradation, surface, and underground water contamination and air pollution (Rösner & van Schalkwyk, 2000; Beaudry, 2018).

While many tailings dumps are undergoing reclamation, their contaminated paths still pose a serious threat to the ecosystem. An approximated 1.6 million South Africans due to various circumstances find shelters in informal and formal settlements that are on – or directly next to – tailings dumps (Nkosi, 2018). Often, inhabitants within the proximity of tailings dams inhale dust contaminated with trace metals and radioactive materials.

Due to gold and uranium occurring in the same geologic formation, there are an estimated 600,000 tons of radioactive uranium from decades of gold mining in the Gauteng province. In fact, for every 10g of gold excavated, 100g of uranium gets to the surface. Uranium gets into humans and farm animals either via the inhalation of fine dust particles from these tailings, or when mine water seepage enters rivers and groundwater sources. Higher levels of exposure to uranium could result in kidney damage and disease, neurological problems, and cancer (Entwistle *et al*., 2019).

Previous studies revealed that only a small portion of contaminants such as Co, Ni and Zn are mobile in acidic soils which implies that the growth of most plants could be retarded due to the occurrence of phytotoxic elements in the topsoils, thus complicating attempts at rehabilitation of tailings dumps (Caporale & Violante, 2016). Furthermore, sediments from tailings dams often contain anomalous trace element concentrations which serve as pools for future contamination. Depletion of buffer minerals, and the subsequent acidification of the subsoil could result in the remobilization of contaminants from the subsoil into the groundwater system in the long term.

A better understanding of the parameters which control the balance between retention and mobility of contaminants in soils is required. Thus, a mandatory risk assessment approach is required for all tailings dumps and reclaimed sites. This will help in the identification of sites, which need rehabilitation and to define the type and extent of remedial measures. Basic rehabilitation requirements at reclaimed sites could consist of soil management strategies such as liming and the addition of organic material to curb the migration of contaminants from the topsoil into the subsoil and groundwater as well as to provide apt conditions for vegetation growth and subsequent land use. Removal of remaining tailings and excavation of those portions of the soil, which are excessively contaminated, are necessary. A well-engineered soil and vegetation cover will be required for tailings dumps that pose a high risk to the environment to limit rainfall infiltration into the impoundment, and thus to reduce the oxidation of sulphide-bearing minerals such as pyrite. Long-term monitoring is an absolute prerequisite for successful rehabilitation, and therefore the safe use of land and water.

This research will no doubt add to the existing body of knowledge on mining and its associated implications to the ecosystem.

1.2 Hypothesis.

It is generally hypothesized that irrespective of the target minerals and pretreatment of the different mine tailings before disposal at specific dumps as seen across the mining areas of the Republic of South Africa. There are increasing environmental challenges such as pollution and contamination of agricultural soils, surface, and sub-surface water sources as well as the atmosphere via fine particle dust all of which impact adversely on the ecosystem due to their mode of deposition, composition, action of erosion and exposure to severe weather.

1.4 Research Aim and Objectives.

1.4.1 Aim.

This study is aimed at investigating the possible environmental and human risks of gold mine tailings dumps over time, as well as the risk of ecological receptors associated with contaminated soils.

1.4.2 Objectives.

To accomplish the aim stated above, the objectives of the intended study are:

- To identify the nature and extent of contamination in unsaturated and saturated zones underneath reclaimed gold mine tailings dumps.
- To assess the potentially adverse environmental effects of residual contaminants in the soils underlying tailings dams with respect to future land use of reclaimed sites.
- Investigate the efficiency of *Hyparrhenia hirta* as a phytoremediator of the gold mine tailings dumps.
- To evaluate and define the existing state of knowledge regarding the long-term environmental impacts of tailings dumps on the subsurface.
- Assessment of water quality in surrounding areas.

1.5 Scope of the Study.

The mine tailings dumps have grasses growing on them, with cows foraging on the grasses. With the aid of hand auger, representative mine tailings shall be collected, and subsequently processed using various analytical techniques such as X-ray fluorescence (XRF) spectrometer, X-ray Diffraction (XRD) and Inductively coupled plasma - optical emission spectrometry (ICP-OES). The grasses growing on the tailings dump shall also be processed accordingly using the same techniques to ascertain possible accumulation of trace metals and the exposure potentials to grazing animals. Aspects of the study involve the collection of water samples from wetlands and surrounding rivers up until Karen Beef farm. This is to ascertain the quality of water available to farmers.

1.6 Study site.

South Africa lies in the southernmost part of the African continent and is known to have a renowned varied topography, great natural beauty, and cultural diversity. It is a medium-sized country, with a total land area of 1,219,090 square kilometers. Ekurhuleni falls within the East Rand region and is characterized by rainfall known to be typical to the Highveld summer rainfall, which occurs from October to April. The average annual rainfall varies from 715 mm to 735 mm an indication that the study area has a distinct moisture deficit. Frost does occur frequently from mid-April to September, which makes temperatures below freezing common during winter times. This area is home to mild summers with temperatures seldom above 30 ºC. During spring and winter, northerly and north-westerly winds occur and during summer north-easterly to north-north-easterly winds occur (EMM, 2007).

There are many pans across the Ekurhuleni area. These pans cover a total area of 3,559 hectares within the Ekurhuleni Metropolitan Municipality area and are mostly seasonal. There are also a few lakes created by mines, which are used for recreational parks. Germiston Lake, Benoni Lake, and Boksburg Lake are the three main lakes used for recreational purposes within the Ekurhuleni Metropolitan Municipality area, but which fall outside the East Rand Basin area. The tailings dump is located along Outeniqua Road & Cloverfield Weg in Springs, Ekurhuleni with some informal settlements within its proximity characterized with subsistence farming amongst the dwellers.

References.

Beaudry, F. 2018. Mine Tailings and the Environment.

Capel, J. 2012. Mining is destroying SA's environment, Benchmarks Foundation.

Caporale, A.G., Violante, A. 2016. Chemical Processes Affecting the Mobility of Heavy Metals and Metalloids in Soil Environments. In: Land Pollution (Hettiarachchi, G. Section Editor), Current Pollution Reports, 2 (1), 15–27.

Ebenebe, P.C., Shale, K., Sedibe, M., et al. 2017. South African Mine Effluents: Heavy Metal Pollution and Impact on the Ecosystem. International Journal of Chemical Sciences, 15 (4), 198.

Ekurhuleni Metropolitan Municipality (EMM). 2007. Environmental management framework for Ekurhuleni. Ekurhuleni.

Entwistle, J.A., Hursthouse, A.S., Marinho Reis, P.A., Stewart, A.G. 2019. Metalliferous Mine Dust: Human Health Impacts and the Potential Determinants of Disease in Mining Communities. In: Human Health Effects of Environmental Pollution (Makris, K.C. Section Editor), Current Pollution Reports, 5 (3), 67–83.

McCarthy, T.S. 2011. The impact of acid mine drainage in South Africa. South African Journal of Science. 107 (5/6), Art. #712.

Nkosi, V. 2018. How mine dumps in South Africa affect the health of communities living nearby. South African Medical Research Council.

Ochieng, G.M., Seanego, E.S., Nkwonta, O.I. 2010. Impacts of mining on water resources in South Africa: A review, Scientific Research and Essays, 5 (22), 3351-3357.

Rösner, T., van Schalkwyk, A. 2000. The environmental impact of gold mine tailings footprints in the Johannesburg region, South Africa, Bulletin of Engineering Geology and the Environment, 59 (2), 137-148.

CHAPTER 2

LITERATURE REVIEW

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Toxic Metal Implications on Agricultural Soils, Plants, Animals, Aquatic life and Human Health: A review.

2.0 Abstract.

The problem of environmental pollution is a global concern as it affects the entire ecosystem. There is a cyclic revolution of pollutants from industrial waste or anthropogenic sources into the environment, farmlands, plants, livestock and subsequently humans through the food chain. Most of the toxic metal cases in Africa and other developing nations are as a result of industrialization coupled with poor effluent disposal and management. Due to a widespread of mining activities in South Africa, pollution is a common site with devastating consequences on the health of animals and humans likewise. In recent years, talks on toxic metal pollution had taken center stage in most scientific symposiums as a serious health concern. Very high levels of toxic metals have been reported in most parts of South African soils, plants, animals, and water bodies due to pollution. Toxic metals such as Zinc (Zn), Lead (Pb), Aluminium (Al), Cadmium (Cd), Nickel (Ni), Iron (Fe), Manganese (Mn), and Arsenic (As) are major mining effluents from tailings which contaminate both the surface and underground water, soil and food, thus affecting biological function, endocrine systems and growth. Environmental toxicity in livestock is traceable to pesticides, agro-chemicals and toxic metals. In this review, concerted efforts were made to condense the information contained in literature regarding toxic metal pollution and its implications in soil, water, plants, animals, marine life and human health.

Keywords: Trace metals - contamination - toxicity - human health.

2.1 Introduction.

The overwhelming discharge of harmful contaminants into the environment as a result of escalated urbanization and industrialization remains an issue of interest in an era of reported climate change.

There is a widespread ecological and global public health concern related to the contamination of the ecosystem on the account of toxic metals. Humans have been further exposed to these toxic metals that emanate from various industrial, agricultural, domestic and technological processes (Arruti *et al*., 2010). Renowned sources of toxic metals in the environment include agricultural, pharmaceutical, atmospheric, industrial, domestic effluents, and geogenic activities (Sträter *et al*., 2010). A number of studies reported on the environmental challenges from these point source areas (Bradl, 2002; He *et al*., 2005).

Despite the natural occurrence of these toxic elements within the earth's crust, anthropogenic activities such as mining, electro-plating, smelting operations, domestic and agro-allied industries are responsible for environmental contamination and human exposure to toxic metals (He *et al*., 2005). Natural phenomena such as weathering and volcanic eruptions have been observed to be sources of toxic metal pollution (Bradl, 2002; He *et al*., 2005), While metal processing in refineries, coal burning in power plants, petroleum combustion, nuclear power stations, microelectronics, wood preservation and paper processing plants are some of the important industrial sources (Arruti *et al*., 2010; Sträter *et al*., 2010). Environmental degradation is a common occurrence in point source areas such as mining, foundries and smelters, and other metal-based industries (Bradl, 2002; He *et al*., 2005). So far, it has been demonstrated that toxic metals in the environment have multiple sources, but the purpose of this review is on mine tailings.

The economies of countries with intense anthropogenic activities such as mining are reported to be favourable, however, there are devastating implications to the environment and human health in a long run (Fashola *et al*., 2016). Mining related operations generate excessive waste materials in the forms of debris and tailings and are subsequently released into the environment (Alder & Rascher, 2007). These wastes are composed of both harmful and toxic metals with certain noble metals. Toxic metal is usually a generic term used to describe any natural occurring metal that could neither be degraded nor destroyed but specifically known to be toxic to humans, and these include, antimony, arsenic, beryllium, bismuth, cadmium, lead, mercury, nickel (Okereafor *et al*., 2017). Due to inadequate skills, technology, and poor management, the ecosystem becomes the receptor of these waste materials.

Contaminated waters by acid mine drainage results in colour changes and turbidity due to the high concentration of trace metals. Nevertheless, there are instances where contamination is not easily detectable to the naked eyes, which accounts to some extent the inability to notice its occurrence. Toxic metals such as Cu, Zn, Co, Ni, Fe, Cr, Mn, I, and Se widely known as micronutrients play a crucial role in the metabolic and physiological activities of humans, plants as well as microorganisms depending on their concentrations. On the other hand, specific toxic metals such as As, Ag, Hg, Cd and Pb are of no biological relevance to plants and animals, rather they are harmful. At higher concentration levels, these elements pollute the environment resulting in deleterious health implications for humans, plants and animals (Vousta *et al*., 1996; Sharma *et al*., 2004; Ebenebe *et al*., 2017). Being noxious and containing carcinogenic metalloids, toxic metals could result in cancer of the skin, lungs and urinary tract disorders; cardiovascular diseases; neurotoxicity; as well as diabetes (Choong *et al*., 2007; Akpor & Muchie, 2010; Acosta *et al*., 2015).

Based on the above, this review article seeks to address some of the environmental health challenges in places with previous and on-going mining activities in a bid to ensuring better practices in current mine processes to safeguard our environment. In addition, this review seeks to bring public awareness on the effects of tailings on human lives and the environment, such that legislative bodies can be pressured to develop stricter legislative frameworks on tailing management.

2.2 The description of mine tailings and tailings dam.

The materials that are left over in the form of liquid, solid, or a slurry of very fine particles upon successful separation and processing of minerals (elements) of interest from an ore are collectively termed mine tailings (DME, 2002). Often, tailings are of no financial benefits to mining firms. They are composed of fine particles suspended in water, with the potential of causing havoc to the environment through the release of trace elements, causing surface run-offs and sinkholes, and contamination of the environment. These materials are very distinct from the usual mine overburden, which includes the soil and rock that is removed to gain access to the ore deposits in open pit mines (Fraser Institute, 2012; Ndlovu *et al*., 2017) and waste rocks, which are rocks that are mined, but containing minerals in very low concentrations to be extracted at a profit and are, therefore, removed ahead of processing (IIED, 2002).

In mining, the steps taken for product extraction are not always efficient, thus creating challenges in recovering reusable and expended processing reagents and chemicals. Most of the unrecoverable and uneconomic metals, chemicals and process water are disposed, largely as slurries, to a final storage area known as a Tailings dam (TD).

In most cases, tailings are pumped at very high pressure into ponds for sedimentation to occur. As a cost saving venture, the water ejected from such mine tailings dams are often employed in other processing cycles at the mines. Mine tailings are regularly stored in tailings dam. Despite not having the exact number of global tailings dams, when poorly designed, constructed or managed, they pose a significant risk to local communities and ecosystems, particularly in downstream environments. The construction of such retaining structures is exclusive and dependent on the type of environment and mineral processing operation.

2.3 The production of mine tailings.

The disposal of mining wastes is one of the sources of environmental impact for many mining exploration activities due to the generated volume of wastes exceeding the actual in-situ total volume of processed ore (Vick, 1990). In recent times, there have been the continued increase in this trend following the demand for more minerals and metals (Jakubick *et al*., 2003). Currently, the volume of tailings being produced by industries are at an alarming rate of over 173.64 billion tons. The production of these tailings and the challenges associated with their storage could be linked to the mineral processing techniques being adopted by individual mines.

Run of mine (ROM) ores get reduced physically through processes such as crushing and grinding. However, the extent of grinding is solely dependent on the metallurgical methods applied in the removal of the economic product. A suitable extraction method is based on a series of mineralogical investigation which could reveal other minerals of economic relevance. In addition, such investigations reveal the quantities and type of reagents that are best suited in separating the concentrates (target elements/minerals) from the gangue (unwanted) materials and the appropriate storage methods for the tailings (Ritcey, 1989). Processing reagents and characteristics of mine tailings such as particle size may be determined using several plant tests. Although, these series of tests may not be a true representation of the final tailings generated from the operational full-scale plant. This implies that there is a provisional design of tailings dam which gets confirmed when there is an actual production of tailings (Blight, 2001).

Concentration is a metallurgical process of extracting the economic product from the crushed and ground ore, leaving behind unwanted materials or wastes often referred to as tailings (Maya *et al*., 2015). As the first step in the mineral processing sequence, Froth flotation involving the use of chemical reagents is a common concentration technique while gravity and magnetic separation are other methods utilized (Vick, 1990). In gold processing, for instance, gravity separation is employed in recovering the coarser particles, while leaching is applied for the finer fractions (EC, 2004).

2.4 Characteristics of mine tailings.

Tailings characteristics are unique and may be attributed to several factors. Often, sediments from mine tailings portray physical and chemical properties that are like specific river sand and silt. The determination of the actual properties of tailings are based on geochemistry, nature and mineralogy of the ore coupled with the processes utilized in extraction of various economic products (Davies & Rice, 2001; Franks *et al*., 2011). There have been reported cases of tailings possessing different mineralogy despite being generated from the same source (Ritcey, 1989). A gold mine tailing for instance, exhibit weak aggregation, limited cohesion potential which results in different moisture level and temperature, high hydraulic conductivity and fine texture which makes them different from the soil (Vega *et al*., 2004; Blight & Fourie, 2005).

From a chemical standpoint, gold tailings have high salinity and are composed of 6 % pyrite with very little organic matter (Vega *et al*., 2006). High acidity together with high metal levels in ground water within the proximity of gold tailings is due to high sulphide content (Vega *et al*., 2004). In terms of pH values, tailings from Iran were reported to be 7.35 (Rafiei *et al*., 2010), 3.25 – 6.28 in

South Africa (Mitileni *et al*., 2011; Okereafor *et al*., 2019) while in India it was 3.48 – 8.12 (Harish & David, 2015).

In order to ascertain the likely dangers associated with tailings when deposited in a storage facility, a consideration of its characteristics cannot be over-looked. Upon the determination of the distinct features of the generated tailings, an appropriate design requirement may be recommended to alleviate environmental effect while encouraging suitable operational routines.

The water balance of a mining project from a design perspective is influenced by the liberation of water and tailings discharge into a storage facility and the subsequent volume that is available for return pumping to the processing plant. The liberation potential is dependent on the physical properties of the tailings which may be estimated based on different laboratory tests.

As a pre-requisite to determining the design requirements of a mine tailings storage facility, certain properties such as chemical composition, physical composition and stability, behaviour under pressure and consolidation rates, erosion stability, settling, drying time and densification behaviour after deposition of the tailings need to be established (EC, 2004). In most cases, the degree of thickening coupled with the method of deposition influences the engineering characteristics of tailings.

It is therefore pertinent to ensure that while investigating the properties of tailings, that physical features and material parameters such as beach slope angles, particle size segregation and water recovery that can occur as a result of varied deposition techniques be identified (SANS, 1998).

2.5 Management of mine tailings.

Mine tailings are often stored on the surface (within retaining structures or in dry stacks) or underground (voids) by a process known as backfill which provides ground and wall support, improve ventilation, substitute for surface tailings storage and prevent subsidence (EC, 2004). The problems emanating from tailings storage facilities are on the rise. Recent technological developments encourage the exploitation of lower grade ores, thus resulting in the generation of higher volumes of tailings that require safe storage. The continued review of global environmental regulations is creating stiffer requirements for various stakeholders within the mining industry on best tailings storage practices. Many historical tailings related incidents could be attributed to poor day to day management, which has led to the strengthening of regulations controlling today's tailings storage facilities (EC, 2004). The parameters that influence stability, operation and management of tailing facilities have been identified and presented together with their methods of control, intervention and mitigation. A free novel online database called TailPro (www.tailpro.com) have been developed to assist tailings personnel in the implementation of a tailings management system more efficiently and effectively.

Certain factors which impact on the site selection, storage and tailings discharge methods adopted are considered in the design of a tailings storage facility (Ritcey, 1989). The environment and ground conditions constitute the major parameters that influence tailings storage design, operation and management. On account of this, a range of other methods of tailings storage and discharge techniques need to be considered when designing a facility for a location. In industry, this is achieved by implementing a trade-off study, usually during the pre-feasibility stage of project development. A selection of options from this study can be taken through to the feasibility stage to assess environmental, social, economic and associated risk and operational factors with a higher level of confidence.

2.6 Ecotoxicity.

Many pollutants including mining wastes, chemical, and organic fertilizers, pesticides, industrial wastes, and other materials are held in soils which often contribute to water and air pollution. Since soil is a key component of environmental chemical cycles, the quality of soil and climate determine the level of agricultural productivity (Bruulsema, 2018; Drobnik *et al*., 2018).

Ecotoxicological tests are complementary tools used to chemically analyze soil contamination. Assessment of the behaviour and toxicity of soil elements, or compounds, should not be based solely on chemical indices. The inclusion of biological indicators in such investigations will aid in better understanding of the behaviour of chemicals in the environment (Wang *et al*., 2018). Terrestrial ecotoxicology attempts at revealing some of the deleterious, morphological, behavioural, physiological, biochemical, and cytogenetic consequences of the discharge into the environment of potentially toxic elements on organisms (Souza *et al*., 2014; Wang *et al*., 2018).

Soil fauna such as Collembola, earthworms , nematodes and enchytraieds are known as bioindicators. They indicate environmental changes at their early stages and identify several modifications types before such changes become drastic, besides determining the pollution types capable of affecting a given ecosystem.

In addition, these organisms play crucial roles in monitoring and management of soil. The use of bioindicators in monitoring programs helps to detect environmental changes at their early stages or the effectiveness of measures taken to improve environmental quality (Souza *et al*., 2014).

2.7 Metal toxicity.

Most metabolic and physiological processes in plants and animals (humans and microorganisms) are influenced by toxic metals (Teresa *et al*., 1997). Some potentially toxic metals such as Cu, Co, Zn, Ni and Cr serves as both micronutrient and vital ingredients in redox processes. These metals through osmotic pressure regulation, electrostatic interactions and cofactor support the stabilization of molecules for many enzymes. Thus, the essential role of toxic metals in intricate biochemical processes (Bruins *et al*., 2000). Ag, As, Cd, Pb and Hg which are non-essential toxic metals are of little or no significant biological relevance to humans and animals rather are highly noxious when noticed in the environment. Studies using culture dependent and independent approaches revealed high concentration levels of toxic metals in mining effluents impacts on the diversity, population size, and the microbial community (Bajkić *et al*., 2013; Xie *et al*., 2013; Xie *et al*., 2016).

Metal toxicity is a widely reported environmental health problem that is dangerous due to bioaccumulation via the food chain which could result in hazardous implications in humans and animals (Aschner, 2002; Aycicek *et al*., 2008). The hazardous effects of toxic trace metals (elements) are dependent on certain factors such as the dietary concentration of the elements, absorption of such elements by the system, homeostatic control of the body for such elements, and the species of the animal involved (Rajaganapathy *et al*., 2011). In addition, the oxidation state of a toxic metal plays a role in the toxicological and biological effects to the environment. Metal toxicity could be attributed to changes in the conformational structure of nucleic acids, proteins or by interference with oxidative phosphorylation and osmotic balance (Yao *et al*., 2008). Toxic metals from industrial and electronic wastes contaminate the entire environment. Cd, Pb, Zn and Hg are some of the toxic metals of deleterious effects to humans and animals alike.

2.8 Potentially toxic metals in soil and their implications.

Several studies into soil contaminants from anthropogenic activities in different geographical locations had been undertaken of which the findings revealed, alarming levels of soil heavy or trace metals which are said to be Chemical Time Bombs (CTBs) (Wood, 1974). The quality of a soil contributes to both enzymatic and microbial activities (Lee *et al*., 1996; Chao *et al*., 2014). The extent of soil contamination could be evaluated using microbial biomass as an important indicator (Aceves *et al*., 1999). There is a significant inhibition of microbial activity in any soil with the problem of toxic metal contamination. In a study of soil contaminated by Cu, Zn, Pb and other toxic metals, a lower microbial biomass was observed within soil nearer to a mine compared to those that are far away from the mine (Kandeler *et al*., 1997). The relationships between the level of toxic metals and how they impact soil microbial biomass have been studied and reveals that low levels of toxic metals support microbial growth which increase microbial biomass; while high concentrations could decrease soil microbial biomass expressively (Fliepbach *et al*., 1994; Chander *et al*., 1995). This trend is likewise applicable to enzymatic activities of soil.

The presence of mine tailings in soil leads to acidification. This is because the toxic metal ions are normally contained in untreated mine tailings. Low pH tailings, i.e. acidic tailings, contain higher amount of toxic metals as compared to high pH tailings. At high pH, most of the toxic metal ions form insoluble hydroxides and sulphides which then precipitate to reduce the ion content of the mine tailings (Percival *et al*., 1999; Speira *et al*., 1999; Yu *et al*., 2006; Jiang *et al*., 2012; Fan *et al*., 2014;). The chemistry and bioavailability of certain elements are likely to be altered as a result of the sudden reduction in pH. Toxic metal such as Cr (III) that is characterized by a high ionic charge, is most likely to be adsorbed on soil exchange sites to the soils with a relatively high cation exchange capacity (CEC). Among the widely known toxic metals, Cu (II) and Pb (II) have a greater tendency (after Cr) to be specifically adsorbed on soil and separated out from Cd, Ni and Zn (Santanu & Chumki, 2018).

In addition, the absorption of soil toxic metals by plants is not always a problem in the interim but becomes something to worry about in the long-term. This is when the concentrations of these toxic metals become too high and have exceeded the permissible limit, which result in plant poisoning and subsequent death. Researchers in Florida, USA, observed that citrus seedlings were severely affected in soil with copper content of more than 50 mg/kg, while the withering of wheat occurred at an increased level of 200 mg/kg (Zhang *et al*., 1989). In a similar fashion, there was retarded growth and development patterns in the seedlings of bean and cabbage at Cd concentration of 30 μ mol/ L (Qin *et al*., 1994). There are reports indicating that Cd in soil may result in poor photosynthesis and protein synthesis in crops, thus damaging cell membranes (Acar & Alshawabkeh, 1993; Kale, 1993). Higher concentrations of Zn in soil suppresses plant metabolic activities, thus resulting in stunted growth and senescence.

The health of humans suffers danger when soils have excessive levels of toxic metals. This is attributable to absorption of toxic metals via the skin, dust inhalation and the pollution of food, water and air that constitutes the food chain. In a test conducted in China on the level of Pb in the blood of children, it was found that over 30 % of the sampled cases had Pb that exceeded the standard home requirement (100 g/L); which was linked with the soil dusts (Robert & Jones, 2009). The Agency for Toxic Substances Management Committee (ATSMC) outlined Cd as the world's sixth most harmful substance that destroys human health (Yabe *et al*., 2010). The metabolism of Calcium is interrupted by Cd which causes calcium deficiency thus resulting in bone fractures and cartilage diseases (Ross *et al*., 2011).

2.9 Potentially toxic metals in water and their implications.

Globally, water contamination from toxic metals has remained a nightmare following the increasing death as a result of diseases linked to contaminated drinking water. Efforts by various environmental and enforcement bodies in effectively controlling the activities that act as sources of these metals have been fruitless (WHO, 1995). Most biological activities have been seriously impeded as a result of these non-essential metals. Generally, the quality of water is compromised due to the presence of toxic metals which are toxic at very high concentration, thus impacting adversely on the health of humans, animals and plants.

In South Africa, water is a scarce commodity with over 70 % of what is being provided by the government for usage in both rural and urban areas emanating from sources like rivers, streams, lakes, ponds and springs (DWAF, 2004). In recent times, the Environmental Mining Council of British Columbia (EMCBC), proposed for a concerted effort towards the safety of the purity and quantity of water against reckless mineral exploration which could compromise the overall quality of water, via increased pollution and sedimentation loads, resulting in poor water quantity which conforms to the principal of sustainable development (EMCBC, 2001; IIED, 2002).

Studies conducted on untreated sewage in Musi river, Hyderabad, India; severe contamination levels by Cd, Ni, Pb, Co, Zn, and Cu with mean content of 0.025, 0.062, 0.210, 0.053, 0.003 and 0.011 ppm, respectively were observed (Raj *et al*., 2006). These values were of serious concern as they exceeded the stipulated permissible limits of WHO (Okereafor *et al*., 2017). A similar study carried out in South Africa, investigated the possible transportation of toxic metals and ground erosion during heavy rainfall in the Rural Mhangweni (Tzaneen, Limpopo province) and reported disturbing toxic metal concentrations such as Al (6.141 ppm), Zn (0.431 ppm), Fe (5.072), Cu (1.506), Pb (2.041) and Mn (3.918 ppm), which surpassed the maximum acceptable level of water composition as stipulated by the United States Environmental Protection Agency (Okereafor *et al*., 2017).

Toxic metal such as Hg is harmful particularly to humans when present in water that forms part of the food chain, this is due to the possibility of the central nervous system being attacked by it, thus leading to Minamata disease (Gibb & O'Leary, 2014; Basu *et al*., 2015). The importance of Zn as a major constituent of many enzymes involved in metabolic reactions as well as the production of hormones cannot be overlooked. However, when excessively consumed by humans may lead to severe abdominal pain, intense vomiting, collapse, and deteriorating changes in the liver (Bahnasawy *et al*., 2011). With devastating lifetime effects, lead poisoning from water had been linked to stunted growth in children, damage of the nervous system, learning disabilities and recently crime and anti-social behaviours (Kumar *et al*., 2013).

2.10 Potentially toxic metals in plants and their implications.

Just like animals and other living organisms, plants show some reactions towards the availability and seldom lack of critical micronutrients, due to the many roles they play in metabolic processes. When these metal ions are limited or not readily available for plant uptake, they result in deficiency in growth, whereas when in excess such as Cd, Hg, As, Pb and Se are supposedly deleterious. Several factors such as the growing environment; temperature, soil pH, soil aeration, competition between plant species, the root system, the availability of the elements in the soil, the type of leaves, and soil moisture are important in the uptake of metals by plants (Nagajyoti *et al*., 2010). On account of the environment of cultivation, previous studies revealed that an increase in pH, i.e., the environment becoming more alkaline, with a corresponding decrease in Eh (redox potential), i.e., the environment being more alkaline, abruptly reduce the amount of toxic metals that are available to plants (Misra & Mani, 1991).

The detrimental effects of excessive toxic metals towards plant growth had been widely documented (Moustakas *et al*., 1994; Ghani, 2010; Masindi & Muedi, 2018; Okereafor *et al*., 2019). Mn, Pb, Cd, Cr and Co during a study were observed to be responsible for the poor growth of maize plants (Zea mays L.) (Ghani, 2010). At extreme levels, toxic metals could result in oxidative stress in plants, mutilation of cell structure through the substitution of deficient elements with toxic metals, and slow down photosynthetic processes in plant cells (Van Assche & Clijsters, 1990). The phytotoxicity effect of Zn and Cd is seen by retarded growth and development, metabolism and an inductive oxidation damage in various plant species such as Brassica juncea (Prasad *et al*., 1999; Doncheva *et al*., 2001). At very high concentrations, Cd and Zn could result in oscillation in catalytic proficiency of enzymes in pea plants (Romero-Puertas *et al*., 2004). Zinc toxicity has been linked to restricted growth of both root and shoot in plants (Fontes & Cox, 1998) as well as chlorosis in newer leaves (Ebbs & Kochian, 1997). There are reported cases of reduced crop production due to Ni toxicity that impaired certain enzymatic activities (amylase, protease and ribonuclease), thus, adversely affecting the germination of seeds. Also affected by Ni were activities such as membrane stability, nitrate reductase and carbonic anhydrase (Yusuf *et al*., 2012).

As a micronutrient for plants, Cu is crucial in the synthesis of ATP and assimilation of CO_2 (Thomas *et al*., 1998). Cu constitutes a major part of proteins such as plastocyanin of photosynthetic system and cytochrome oxidase of respiratory electron transport chain (Demirevska-Kepova *et al*., 2004). When in excess as a result of anthropogenic activities such as mining, Cu has a cytotoxic effect on soil which induces stress and causes growth retardation and leaf chlorosis in plants (Lewis *et al*., 2001). Oxidative stress in plants as a result of high levels of Cu results in the disturbance of metabolic pathways and damage to macromolecules (Hegedus *et al*., 2001). From previous studies, Copper toxicity were reported to have affected the growth of *Alyssum montanum* (Ouzounidou, 1994) while a combination of both Cu and Cd were responsible for the poor germination, seedling length and number of lateral roots in *Solanum melongena* (Neelima & Reddy, 2002).

Occurring in several forms, HgS, Hg^{2+}, Hg° and methyl-Hg; Mercury (Hg) is known to accumulate in higher and aquatic plants (Kamal *et al*., 2004; Wang & Greger, 2004; Israr *et al*., 2006). It is reported that higher concentrations of Hg^{2+} is strongly phytotoxic to plant cells, inducing visible injuries and physiological disorders in plants such as the closure of leaf stomata and physical obstruction of the flow of water (Zhang & Tyerman, 1999; Zhou *et al*., 2007). There are observed interferences in the mitochondrial activity of plants as a result of high levels of Hg^{2+} which results in the disruption of biomembrane lipids and cellular metabolism (Messer *et al*., 2005; Cargnelutti *et al*., 2006).

Lead (Pb) exerts detrimental effects on the morphology, growth and photosynthetic processes of plants through interference with vital enzymes, thus inhibiting seed germination (Sudhakar *et al*., 1992; Sharma & Dubey, 2005). Oxidative stress is another complication as a result of higher concentrations of Pb which increases the production of reactive oxygen species (ROS) in plants (Reddy *et al*., 2005).

It is noteworthy to mention that there are plants known as accumulators that can withstand higher concentrations of trace metals in their natural environment. These plants through diverse mechanisms such as (i) exclusion: restriction of metal transport and maintenance of a constant metal concentration in the shoot over a wide range of soil concentrations; (ii) inclusion: metal concentrations in the shoot reflecting those in the soil solution through a linear relationship; and (iii) bioaccumulation: the accumulation of metals in the shoot and roots of plants at both low and high soil concentrations can tolerate high metal levels (Baker, 1981).

A summary of some of the effects of metal toxicity on plants are detailed in **Table 2.1.**

Table 2. 1 Summary of the effects of potentially toxic metal on plants.

Toxic metal	**Plant**	**Toxic effect on plant**	**Reference**
As	Rice (*Oryza sativa*)	Reduced leaf area and dry matter production; reduction in seed germination; decrease in seedling height	(Marin *et al*., 1993; Abedin *et al*., 2002)
	Tomato (*Lycopersicon esculentum*)	Drop in fruit yield; reduction in leaf fresh weight	(Barrachina *et al*., 1995)
	Canola (*Brassica napus*)	Restricted growth; chlorosis; wilting	(Cox *et al*., 1996)
Cd	Wheat (*Triticum sp*.)	Decline in seed germination; reduction in nutrient content of plant	(Yourtchi & Bayat, 2013)
	Garlic (*Allium sativum*)	Reduced shoot development; Cd buildup	(Jiang *et al*., 2001)
	Maize (*Zea mays*)	Reduced shoot development; inhibition of root growth	(Wang *et al*., 2007)
Co	Tomato (*Lycopersicon esculentum*)	Reduction in plant nutrient content	(Jayakumar *et al*., 2013)
	Mung bean (*Vigna radiata*)	Decline in antioxidant enzyme actions; reduction in plant sugar, starch, amino acids, and protein content	(Jayakumar *et al*., 2008)
	Radish (*Raphanus sativus*)	Decline in shoot length, root length, and total leaf area; reduction in chlorophyll content, plant nutrient content, antioxidant enzyme activities, decrease in plant sugar, amino acid, and protein content	(Jayakumar *et al*., 2007)

Table 2.1: Summary of the effects of toxic metal on plants continued.

Toxic metal	**Plant**	**Toxic effect on plant**	**Reference**
Cr	Wheat (Triticum sp.)	Stunted shoot and root growth	(Sharma & Sharma, 1993; Panda & Patra, 2000)
	Tomato (*Lycopersicon esculentum*)	Reduction in plant nutrient acquisition	(Moral *et al*., 1995; Moral *et al*., 1996)
	Onion (*Allium cepa*)	Inhibition of germination process; plant biomass reduction	(Nematshahi *et al*., 2012)
Cu	Bean (*Phaseolus vulgaris*)	Buildup of Cu in plant roots; root malformation and reduction	(Cook *et al*., 1997)
	Black bindweed (*Polygonum convolvulus*)	Plant death; reduced biomass and seed production	(Kjaer & Elmegaard, 1996)
	Rhodes grass (*Chloris gayana*)	Stunted root development	(Sheldon & Menzies, 2005)
Hg	Rice (*Oryza sativa*)	Reduction in plant height; reduced tiller and panicle formation; reduced yield; bioaccumulation in shoot and root of seedlings	(Du *et al*., 2005)
	Tomato (*Lycopersicon esculentum*)	Decrease in the percentage of germination; reduced plant height; reduction in flowering and fruit weight; chlorosis	(Shekar *et al*., 2011)
Mn	Broad bean (*Vicia faba*)	Manganese accumulation in shoot and root; chlorosis.	(Arya & Roy, 2011)
	Spearmint (*Mentha spicata*)	Reduction in the content of chlorophyll and carotenoid.	(Asrar *et al*., 2005)
	Pea (*Pisum sativum*)	Reduction in relative growth rate and photosynthetic activities.	(Doncheva *et al*., 2005)
	Tomato (*Lycopersicon esculentum*)	Slower plant growth; reduction in the concentration of chlorophyll.	(Shenker *et al*., 2004)

Table 2.1: Summary of the effects of toxic metal on plants continued.

Toxic metal	**Plant**	**Toxic effect on plant**	**Reference**
Ni	Pigeon pea (*Cajanus cajan*)	Drop in chlorophyll content and stomatal conductance; decreased enzyme activity which affected Calvin cycle and CO_2 fixation.	(Sheoran *et al*., 1990)
	Rye grass (*Lolium perenne*)	Reduction in plant nutrient acquisition; decrease in shoot yield; chlorosis.	(Khalid & Tinsley, 1980)
	Wheat (Triticum sp.)	Reduction in acquisition of plant nutrient.	(Pandolfini *et al*., 1992; Barsukova & Gamzikova, 1999)
	Rice (*Oryza sativa*)	Stunted root development.	(Lin & Kao, 2005)
Pb	Maize (*Zea mays*)	Reduction in germination percentage; suppressed growth; reduced plant biomass; decrease in plant protein content.	(Hussain *et al*., 2013)
	Portia tree (*Thespesia populnea*)	Drop in number of leaves and leaf area; reduced plant height; decrease in plant biomass.	(Kabir *et al*., 2009)
	Oat (*Avena sativa*)	Inhibition of enzyme activity which affected CO_2 fixation.	(Moustakas *et al*., 1994)
Zn	Cluster bean (*Cyamopsis tetragonoloba*)	Reduction in germination percentage; reduced plant height and biomass; decrease in chlorophyll, carotenoid, sugar, starch, and amino acid content.	(Manivasagaperumal *et al*., 2011)
	Pea (*Pisum sativum*)	Reduction in chlorophyll content; alteration in structure of chloroplast; reduction in photosystem II activity; reduced plant growth.	(Doncheva *et al*., 2001)
	Rye grass (*Lolium perenne*)	Accumulation of Zn in plant leaves; growth reduction; decrease in plant nutrient content; reduced efficiency of photosynthetic energy conversion	(Bonnet *et al*., 2000)

2.11 Potentially toxic metals in Human health and their implications.

A wider population in most developing countries are faced with challenges of toxic metal contamination of dietary substances due to poor legislations on the management of toxic metal sources coupled with plant uptake of metals at high concentrations (D'Souza & Peretiatko, 2002; Cheng, 2003; Meharg, 2004). On account of these metals being ubiquitous and recalcitrant, their admission into the human body poses severe health implications as they could result in the malfunctioning of certain cellular processes through the displacement of essential metals from their respective locations. Toxic metals such as Lead (Pb), cadmium (Cd), mercury (Hg), and arsenic (As) are extensively dispersed in the environment. Unfortunately, there are no known benefits of these metals in humans, as well as any established homeostasis mechanism for them (Vieira *et al*., 2011). In addition to the toxicities of metals, the potential carcinogenicity of metal compounds had been of interest to the society. With a growing working population in the mining industries coupled with human settlements springing forth within the vicinities of mines, the health conditions of individuals in this circumstance are compromised due to continued exposure to various trace metals.

The problem of oxidative deterioration of biological macromolecules has been linked with the binding of metals to DNA and nuclear proteins (Flora *et al*., 2008). Some of the symptoms of metal poisoning in humans within the mining industries include intellectual disability in children, dementia in adults, central nervous system disorders, kidney diseases, liver diseases, insomnia, emotional instability, depression and vision disturbances (Jan *et al*., 2011).

The transportation mechanism of toxic metals in humans is somewhat complex. For instance, Pb ends up in humans mostly via the digestive tract and respiratory tract, before going into the blood circulation in the form of soluble salts, protein complexes or ions with over 95% of the insoluble phosphate lead accumulating in bones. As a highly pro-organizational element, Pb affects and destroys several body organs and systems, such as kidney, liver, reproductive system, nervous system, urinary system, immune system and the basic physiological processes of cells and gene expression (Mahurpawar, 2015). Prolong Lead exposure in children has been linked with neurological damage resulting to a decrease in intelligence, loss of short-term memory, learning disabilities and challenges with general coordination. Prenatal exposure may result in the reduction in immunity and birth weight, which alludes to the claim why some infants are diagnosed with asthma and allergies (Day, 1998). There are suggestions that lead can impact behavioural inhibition mechanisms with a resultant intensification in violence (Masters, 1998), and that it can support tooth decay (Gil *et al*., 1996).

Cu, Zn and Ni on the other hand, are vital trace metals in the human body, but when consumed in excess are deleterious to the body. With a larger population working in the mining industries, the carcinogenic effects of Ni and Cu, both being regarded as tumor promoting metals, had raised international concerns. Prolonged human exposure to Copper often result in severe mucosal irritation and corrosion, capillary damage, hepatic and renal damage, irritation of the central nervous system occasioned with depression. System dysfunctions resulting in the impairment of growth and reproduction are linked with excessive Zinc. A previous study indicated that individuals working closely with nickel powder are at risks of having respiratory cancer, and that the content of Ni in the environment is absolutely associated with nasopharyngeal carcinoma (Barta *et al*., 2019). With symptoms such as uncontrollable shaking, muscle wasting, partial blindness, and deformities in children exposed in the womb, excessive mercury damages the nervous system (Baby *et al*., 2010). There are reports suggesting that at concentrations lower than the stipulated limits of WHO, mercury can damage both the foetal and embryonic nervous systems with consequential learning complications, poor memory and shortened attention spans (Jorgensen *et al*., 1997).

Depending on the severity of the level of exposure, Cadmium (Cd) toxicity is mostly evident in organs such as liver, kidneys, placenta, brain, lungs and bones (Sobha *et al*., 2007). Some of the symptoms of the deleterious effects include nausea, abdominal cramps, vomiting, dyspnea and muscular weakness. Extreme exposure has been linked to death and pulmonary odema with effects such as emphysema, bronchiolitis and alveolitis (Duruibe *et al*., 2007). A variety of clinical conditions such as cardiac failure cancers, anosmia, osteoporosis, cerebrovascular infarction, proteinuria cataract formation in the eyes and emphysema are largely associated with Cadmium.

Just like mercury and lead, the toxicity symptoms of arsenic are dependent on the form in which they are ingested. Arsenic aids the coagulation of protein, formation of complexes with coenzymes and stops the production of adenosine triphosphate (ATP) during respiration. It is mostly carcinogenic in compounds of its oxidation states which results in death when exposed to an extreme level. Cases of arsenic being responsible for disorder similar to, and often likened to Guillain-Barre syndrome, an anti-immune disorder that arises when the body's immune system erroneously attacks part of the PNS, leading to inflammation of the nerve that causes weakness of the muscle (Duruibe *et al*., 2007). A summary of some of the effects of potentially toxic metal on human health are detailed in **Table 2.2**.

Table 2. 2 Summary of the effects of potentially toxic metal on human health.

Toxic metal	Toxic effect on humans	Reference
As	Cancer of the skin, lungs, bladder, prostrate and blood (Leukemia).	(Rossman *et al*., 2004; Smith *et al*., 2006; Duruibe *et al*., 2007; Sobha *et al*., 2007; Meliker *et al*., 2010; Lin *et al*., 2013)
	Neurobehavioral abnormalities during puberty and adulthood.	(García-Esquinas *et al*., 2013; Heck *et al*., 2014)
	Diabetes and cardiovascular disorders.	(Tsai *et al*., 2003; Wasserman *et al*., 2004)
	Increased fetal mortality and preterm birth in pregnancy.	(Nizam *et al*., 2013)
Cd	Shortness of breath, lung edema and destruction of mucous membranes.	(Lee *et al*., 2002)
	Acute vomiting and diarrhoea.	(Hopenhayn *et al*., 2003)
	Kidney and bone damage.	(Seidal *et al*., 1993; Nordberg, 2004)
Co	Decreased pulmonary function, increased frequency of cough, respiratory Inflammation, and pulmonary fibrosis.	(Jin *et al*., 2002)
	Myelopathy, brachial plexus neuropathy and vocal cord paresis.	(Nogawa *et al*., 2004)
	Hearing and visual impairment.	(Sheikh, 2016)

Table 2.2: Summary of the effects of potentially toxic metal on human health continued.

Toxic metal	**Toxic effect on humans**	**Reference**
Cr	Pulmonary irritant effects such as asthma, chronic bronchitis, chronic irritation, chronic pharyngitis, chronic rhinitis, congestion and hyperemia, polyps of the upper respiratory tract, tracheobronchitis, and ulceration of the nasal mucosa with possible septal perforation.	(Johansson *et al*., 2000)
	Irritant and allergic contact dermatitis	(Dayan & Paine, 2001; Leyssens *et al*., 2017)
	Respiratory system cancers such as lungs, nasal and sinus cancers	(Lim *et al*., 2017)
	Acute tubular necrosis and acute renal failure	(Brutti *et al*., 2013)
	Derangement of the liver cells, necrosis, lymphocytic and histocytic infiltration, and increases in Kupffer cells.	(Gibb *et al*., 2000)
	Decreased hemoglobin content and hematocrit, increased total white blood cell counts, reticulocyte counts, and plasma hemoglobin.	(Basile *et al*., 2012)
Cu	Irritation of the nose, mouth, and eyes, headaches, dizziness, nausea, vomiting, stomach cramps, and diarrhea.	(Abdel-Gadir *et al*., 2016)
	Liver and kidney damage and even death.	(Ray, 2016)
	Wilson's Disease that is characterized by hepatic cirrhosis, brain damage, demyelization, renal disease, and copper deposition in the cornea.	(ATSDR, 2004)

Table 2.2: Summary of the effects of potentially toxic metal on human health continued.

Toxic metal	Toxic effect on humans	Reference
Hg	Neurological and behavioural disorders such as tremors, insomnia, memory loss, neuromuscular effects, headaches, and cognitive and motor dysfunction.	(Aston *et al*., 2000)
	Red blood cell accumulation (competes with iron for hemoglobin binding), Inhibits myelin synthesis in developing foetus and children.	(Kodama *et al*., 2012)
	Immune, enzyme, and genetic alterations.	(Bridges & Zalups, 2010; Rice *et al*., 2014)
	Young's syndrome (Azoospermia sinopulmonary infections).	(Andreoli & Sprovieri, 2017)
Mn	Parkinsonian syndromes	(Engwa *et al*., 2019)
	Alteration in cardiovascular function	(Hamada *et al*., 2013)
	Increased infant mortality, hallucinations, forgetfulness and nerve damage.	(Jiang *et al*., 2006)
	Impotence and loss of libido in men	(Jiang & Zheng, 2005)
Ni	Nausea, vomiting, abdominal pain, diarrhea, headache, cough, shortness of breath, and giddiness	(Spangler & Spangler, 2009)
	Death due to nickel-induced Adult Respiratory Distress Syndrome (ARDS), chronic bronchitis, reduced lung function, and cancer of the lung and nasal sinus.	(Meeker *et al*., 2010)
	Allergic skin reaction	(Sunderman *et al*., 1988)
	Genotoxicity haematotoxicity, teratogenicity, immunotoxicity and carcinogenicity	(Rendall *et al*., 1994)

Table 2.2: Summary of the effects of potentially toxic metal on human health continued.

Toxic metal	Toxic effect on humans	Reference
Pb	Headache, loss of appetite, abdominal pain, fatigue, sleeplessness, hallucinations, vertigo, renal dysfunction, hypertension, arthritis, birth defects, mental retardation, autism, psychosis, allergies, paralysis, weight loss, dyslexia, hyperactivity, muscular weakness, kidney damage, brain damage, coma and death	(Das *et al*., 2008)
	Disruption of the intracellular second messenger systems resulting in the alteration of the functioning of the central nervous system.	(Zdrojewicz *et al*., 2016)
Zn	Respiratory disorder from inhalation of zinc smoke, epigastric pains, risk of prostate cancer and lethargy.	(Martin & Griswold, 2009)
	Copper deficiency	(Teo *et al*., 1997)
	Irritation and corrosion of the gastrointestinal tract, acute renal tubular necrosis and interstitial nephritis.	(Barceloux & Barceloux, 1999; Igic *et al*., 2002; Plum *et al*., 2010)

2.12 Potentially toxic metals in aquatic environment and their implications.

As highly persistent and toxic in trace amounts, some metals can induce acute oxidative stress in aquatic animals. Through anthropogenic activities pollutants in the form of pesticides, pharmaceuticals and toxic metals contaminate several water bodies. Of these pollutants, toxic metals are of great danger to the ecology of water body as they influence fish which is a vital protein source. Thus, the ecotoxicological significance of these toxic metal contaminants. Since certain metals are not bacterial degradable, their presence as contaminants in rivers may impact adversely on the ecological equilibrium of aquatic environment, resulting in reduced diversity of marine life (Ayandiran *et al*., 2009; Woo *et al*., 2009).

Histopathological alterations such as interference in the metabolic activities of fish resulting to cellular intoxication and death at a cellular level are brought about by toxic metals. Histological and histopathological changes in critical organs and tissues due to toxic metal pollutants often occur before they produce irreversible effects on the biota. The continuous exposure of fishes to waterborne and particulate toxic metals is as a result of the constant movement of water through gills and through food sources.

Toxic metals have been reported to be responsible for the generation of Reactive Oxygen Species (ROS) which destroys the protein, lipid and DNA content of exposed aquatic animals. Redox active toxic metals (Fe, Cu, Cr etc.) undergo redox cycling while redox inactive toxic metals (such as Pb, Cd and Hg) undergo covalent electron sharing with cells major antioxidant enzymes (Thiols). Both groups of toxic metals result in the production of ROS as hydroxyl radical (OH), Superoxide radical (O_2^{-}) or hydrogen peroxide (H_2O_2) which reduce cells inherent antioxidant defense (Fatima *et al*., 2014). From previous studies, it was reported that several defects such as epithelial lifting, interstitial oedema, leucocytic infiltration, hyperplasia of epithelial cells, lamellar fusion, vasodilatation and necrosis are as a result of toxic metals coming in contact with the large surface area of fish gills (Akan *et al*., 2009; Taweel *et al*., 2011; Fatima & Usmani, 2013). The contamination of fish by toxic metals such as Methylmercury, a toxic chemical form of mercury formed by bacterial methylation of organic mercury is a public health concern as they form part of the food chain (Soliman, 2006).

2.13 Conclusions.

Anthropogenic activities such as mining and its associated metallurgical processes have contributed significantly to environmental deterioration through the improper management of the tailings which contain toxic metals that the mining industries produce. The generated tailings are one of the major metal sources, which can contaminate a variety of ecological settings through particle dispersion during windy periods. During particle dispersion, animals and humans can inhale the tailings particles which contain toxic metals, thus resulting in health-related complications. Some of the devastating effects of these metals on human health include, but not limited to the developmental retardation, cancer, kidney damage, endocrine disruption, immunological and neurological effects, and other disorders. Aquatic organisms suffer damages mostly at a cellular level as a result of extreme toxic metal concentrations. Considering the toxicity and bioaccumulation potentials of toxic metals, strict legislation on tailings management needs to be developed and enforced, such that the above-mentioned negative effects could be curbed.

References.

Abdel-Gadir, A., Berber, R., Porter, J.B., Quinn, P.D., Suri, D., Kellman, P., Hart, A.J., Moon, J.C., Manisty, C., & Skinner, J.A. 2016. Detection of metallic cobalt and chromium liver deposition following failed hip replacement using T2* and R2 magnetic resonance. Journal of Cardiovascular Magnetic Resonance, 18, 29.

Abedin, M.J., Cotter-Howells, J., & Meharg, A.A. 2002. Arsenic uptake and accumulation in rice (Oryza sativa L.) irrigated with contaminated water. Plant and Soil, 240 (2), 311–319.

Acar, Y.B., & Alshawabkeh, A.N. 1993. Principles of electrokinetic remediation. Environmental Science and Technology, 27 (13), 2638-2647.

Aceves, M.B., Grace, C., Ansorena, J., et al. 1999. Soil microbial biomass and organic C in a gradient of zinc concentration in soils around a mine spoil tip. Soil Biology and Biochemistry, 31(6), 867-876.

Acosta, J.A., Arocena, J.M., & Faz, A. 2015. Speciation of arsenic in bulk and rhizosphere soils from artisanal cooperative mines in Bolivia. Chemosphere, 138, 1014–1020.

Adler, R., & Rascher, J. 2007. A Strategy for the Management of Acid Mine Drainage from Gold Mines in Gauteng; CSIR: Pretoria, South Africa.

Agency for Toxic Substances and Disease Registry (ATSDR). 2004. Toxicological profile for Copper.; Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

Akan, J.C., Abdulrahman, F.I., Sodipo, O.A., & Akandu, P.I. 2009. Bioaccumulation of some heavy metals of six freshwater fishes caught from Lake Chad in Doron Buhari, Maiduguri, Borno State, Nigeria. Journal of Applied Sciences in Environmental

Sanitation, 4, 103-114.

Akpor, O.B., & Muchie, M. 2010. Remediation of heavy metals in drinking water and wastewater treatment systems: Processes and applications. International Journal of Physical Science, 5, 1807–1817.

Andreoli, V., & Sprovieri, F. 2017. Genetic Aspects of Susceptibility to Mercury Toxicity: An Overview. International Journal of Environmental Research and Public Health, 14 (1), 93.

Arruti, A., Fernández-Olmo, I., Irabien, A. 2010. Evaluation of the contribution of local sources to trace metals levels in urban PM2.5 and PM10 in the Cantabria region (Northern Spain). Journal of Environmental Monitoring, 12 (7), 1451–1458.

Arya, S.K., & Roy, B.K. 2011. Manganese induced changes in growth, chlorophyll content and antioxidants activity in seedlings of broad bean (Vicia faba L.). Journal of Environmental Biology, 32 (6), 707–711.

Aschner, M. 2002. Neurotoxic mechanism of fishbone methylmetry. Environmental Toxicology and Pharmacology, 12, 101-102.

Asrar, Z., Khavari-Nejad, R.A., & Heidari, H. 2005. Excess manganese effects on pigments of Mentha spicata at flowering stage. Archives of Agronomy and Soil Science, 51 (1), 101–107.

Aston, N.S., Watt, N., Morton, I.E., Tanner, M.S., & Evans, G.S. 2000. Copper toxicity affects proliferation and viability of human hepatoma cells (HepG2 line). Human & Experimental Toxicology, 19 (6), 367-376.

Ayandiran, T.A., Fawole, O.O., Adewoye, S.O., & Ogundiran, M.A. 2009. Bioconcentration of metals in the body muscle and gut of Clarias gariepinus exposed to sublethal concentrations of soap and detergent effluent. Journal of cell and Animal Biology, 3 (8), 113–118.

Aycicek, M., Kaplan, O., & Yaman, M. 2008. Effect of cadmium on germination, seedling growth and metal contents of sunflower (Helianthus annus L.). Asian Journal of Chemistry, 20, 2663-2672.

Baby, J., RAJ, J.S., Biby, E.T., Sankarganesh, P., Jeevitha, M.V., Ajisha, S.U., & Rajan, S.S. 2010. Toxic effect of heavy metals on aquatic environment. International Journal of Biological and Chemical Sciences, 4 (4), 939–952.

Bahnasawy, M., Khidr, A., & Dheina, N. 2011. Assessment of heavy metal concentrations in water, plankton, and fish of Lake Manzala, Egypt. Turkish Journal of Zoology; 35 (2), 271-280.

Bajkic´, S., Naranc˘ic´, T., Đokic´, L., Đord¯evic´, D., Nikodinovic´-Runic´, J., Moric´, I., & Baker, A.J.M. 1981. Accumulators and excluders strategies in the response of plants to heavy metals. Journal of Plant Nutrition, 3, 64–654.

Barceloux, D.G., & Barceloux, D. 1999. Zinc. Journal of Toxicology: Clinical Toxicology, 37 (2), 279-292.

Barrachina, A.C., Carbonell, F.B., & Beneyto, J.M. 1995. Arsenic uptake, distribution, and accumulation in tomato plants: effect of arsenite on plant growth and yield. Journal of Plant Nutrition, 18 (6), 1237–1250.

Barta, J.A., Powell, C.A., & Wisnivesky, J.P. 2019. Global Epidemiology of Lung Cancer. Annals of Global Health, 85 (1), 8.

Basile, D.P., Anderson, M.D., & Sutton, T.A. 2012. Pathophysiology of Acute Kidney Injury. Comprehensive Physiology, 2 (2), 1303–1353.

Basu, A., Phipps, S., Long, R., Essegbey, G., & Basu, N. 2015. Identification of response options to artisanal and small-scale gold mining (ASGM) in Ghana via the Delphi process. International Journal of Environmental Research and Public Health, 12, 11345–11363.

Blight, G.E. 2001. Management and operational background to three tailings dam failure in South Africa. In: Slope stability in surface mining, W. A. Hustrulid, W.A.; McCarter, M.K.; and van Amponsah-Dacosta, D.J.A.; Zyl, F (eds.), Society for Mining, Metallurgy and Exploration, Inc., Littleton. Co. USA., 383-390.

Blight, G., & Fourie, A. 2005. Catastrophe revisited-disastrous flow failures of mine and municipal solid waste. Geotechnical & Geological Engineering, 23, 219–248.

Bonnet, M., Camares, O., & Veisseire, P. 2000. Effects of zinc and influence of Acremonium Lolli on growth parameters, chlorophyll a fluorescence and antioxidant enzyme activities of ryegrass (Lolium perenne L. cv Apollo). Journal of Experimental Botany, 51 (346), 945–953.

Bradl, H, editor. 2002. Heavy Metals in the Environment: Origin, Interaction and Remediation. London: Academic Press; 6.

Bridges, C.C., & Zalups, R.K. 2010. Transport of inorganic mercury and methylmercury in target tissues and organs - Review. Journal Toxicology and Environmental Health B. Critical Review, 13 (5), 385-410.

Bruins, M.R., Kapil, S., & Oehme, F.W. 2000. Microbial resistance to metals in the environment. Ecotoxicology and Environmental Safety, 45, 198-207.

Brutti, C.S., Bonamigo, R.R., Cappelletti, T., Martins-Costa, G.M., & Menegat, A.P. 2013. Occupational and non-occupational allergic contact dermatitis and quality of life: a prospective study. An Bras Dermatol, 88 (4), 670–671.

Bruulsema, T. 2018. Managing nutrients to mitigate soil pollution. Environmental Pollution, 243 (Pt B),1602-1605.

Cargnelutti, D., Tabaldi, L.A., Spanevello, R.M., Jucoski, G.O., Battisti, V., Redin, M., Linares, C.E.B., Dressler, V.L., Flores, M.M., Nicoloso, F.T., Morsch, V.M., & Schetinger, M.R.C. 2006. Mercury toxicity induces oxidative stress in growing cucumber seedlings. Chemosphere, 65, 999–1106.

Chander, K., Brookes, P.C., & Harding, S.A. 1995. Microbial biomass dynamics following addition of metal-enriched sewage sludge to a sandy loam. Soil Biology and Biochemistry, 27 (11), 1409-1421.

Chao, S., LiQin, J., & WenJun, Z. 2014. A review on heavy metal contamination in the soil worldwide: Situation, impact and remediation techniques. Environmental Skeptics and Critics, 3 (2), 24-38.

Cheng, S.P. 2003. Heavy metal pollution in China: Origin, pattern and control. Environmental Science and Pollution Research, 10, 192–198.

Choong, T.S., Chuah, T.G., Robiah, Y.; Koay, F.G.; & Azni, I. 2007. Arsenic toxicity health hazards and removal techniques from water: An overview. Desalination, 217, 139–166.

Cook, C.M., Kostidou, A., Vardaka, E., & Lanaras, T. 1997. Effects of copper on the growth, photosynthesis and nutrient concentrations of Phaseolus plants. Photosynthetica, 34 (2), 179–193.

Cox, M.S., Bell, P.F., & Kovar, J.L. 1996. Differential tolerance of canola to arsenic when grown hydroponically or in soil. Journal of Plant Nutrition, 19 (12), 1599–1610.

D'Souza, C., & Peretiatko, R. 2002. The nexus between industrialization and environment: A case study of Indian enterprises. Environmental Management and Health, 13, 80–97.

Das, K.K., Das, S.N., & Dhundasi, S.A. 2008. Nickel, its adverse health effects & oxidative stress – A Review. Indian Journal of Medical Research, 128, 412–425.

Davies, M.P., & Rice, S. 2001. An alternative to conventional tailings management "Dry stack" filtered tailings. In Proceedings of the Tailings and Mine Waste'01, Fort Collins, CO, USA, 411–420.

Day, M. 1998. Lead in the womb. New Scientist, 7.

Dayan, A.D., & Paine, A.J. 2001. Mechanisms of chromium toxicity, carcinogenicity and allergenicity: Review of the literature from 1985 to 2000. Human & Experimental Toxicology, 20 (9), 439–451.

Demirevska-Kepova, K., Simova-Stoilova, L., Stoyanova, Z., Holzer, R., & Feller, U. 2004. Biochemical changes in barley plants after excessive supply of copper and manganese. Environmental and Experimental Botany, 52, 253–266.

Department of Minerals and Energy (DME). 2002. Mineral and Petroleum Resource Development Bill, Government Gazette, Pretoria, South Africa.

Department of Water Affairs and Forestry (DWAF). 2004. Olifants Water Management Area: Internal Strategic Perspective. Report P WMA 04/0000/00/0304. Department of Water Affairs and Forestry, Pretoria.

Doncheva, S., Georgieva, K., Vassileva, V., Stoyanova, Z., Popov, N., & Ignatov, G. 2005. Effects of succinate on manganese toxicity in pea plants. Journal of Plant Nutrition, 28 (1), 47–62.

Doncheva, S., Stoynova, Z., & Violeta, V. 2001. Influence of Succinate on zinc toxicity of pea plants. Journal of Plant Nutrition, 24 (6), 789–804.

Drobnik, T., Greiner, L., Keller, A., Grêt-Regamey, A. 2018. Soil quality indicators—From soil functions to ecosystem services. Ecological Indicators, 94, 151-169.

Du, X., Zhu, Y.G., Liu, W.J., & Zhao, X.S. 2005. Uptake of mercury (Hg) by seedlings of rice (Oryza sativa L.) grown in solution culture and interactions with arsenate uptake. Environmental and Experimental Botany, 54 (1), 1–7.

Duruibe, J.O., Ogwuegbu, M.O.C., & Egwurugwu, J.N. 2007. Heavy metal pollution and human biotoxic effects. International Journal of Physical Sciences, 2 (5), 112–118.

Ebbs, S.D., & Kochian, L.V. 1997. Toxicity of zinc and copper to Brassica species: implications for phytoremediation. Journal of Environmental Quality, 26, 776–781.

Ebenebe, P.C., Shale, K., Sedibe, M., Tikilili, P., & Achilonu, M.C. 2017. South African Mine Effluents: Heavy Metal Pollution and Impact on the Ecosystem. International Journal of Chemical Science; 15 (4), 198.

Engwa, G.A., Ferdinand, P.U., Nwalo, F.N., & Unachukwu, M.N. 2019. Mechanism and Health Effects of Heavy Metal Toxicity in Humans. In: Poisoning in the Modern World - New Tricks for an Old Dog? Edited by Karcioglu O and Arslan B. IntechOpen, DOI: 10.5772/intechopen.82511.

Environmental Mining Council of British Colombia (EMCBC). 2001. Acid mine drainage: mining and water pollution issues in British Colombia.

European Commission (EC). 2004. Draft Reference Document on Best Available Techniques for Management of Tailings and Waste-Rock in Mining Activities. European Commission, Edificio EXPO, Seville, Spain: 563.

Fan, J., He, Z., Ma, L.Q., Yang, Y., & Stofella, P. J. 2014. Impacts of calcium water treatment residue on the soil-water-plant system in citrus production. Plant Soil, 374, 993–1004.

Fatima, M., Usmani, N., & Hossain, M.M. 2014. Heavy Metal in Aquatic Ecosystem

Emphasizing its Effect on Tissue Bioaccumulation and Histopathology: A Review. Journal of Environmental Science and Technology, 7, 1-15.

Fatima, M., & Usmani, N. 2013. Histopathology and bioaccumulation of heavy metals (Cr, Ni and Pb) in fish (Channa striatus and Heteropneustes fossilis) tissue: A study for toxicity and ecological impacts. Pakistan Journal of Biological Sciences, 16, 412-420.

Fashola, M.O., Ngole-Jeme, V.M., & Babalola, O.O. 2016. Heavy Metal Pollution from Gold Mines: Environmental Effects and Bacterial Strategies for Resistance. International Journal of Environmental Research and Public Health, 13, 1047.

Fliepbach, A., Martens, R., & Reber, H. 1994. Soil microbial biomass and activity in soils treated with heavy metal contaminated sewage sludge. Soil Biology and Biochemistry, 26, 1201-1205.

Flora, S.J.S., Mittal, M., & Mehta, A. 2008. Heavy metal induced oxidative stress and its reversal by chelation therapy. Indian Journal of Medical Research, 128, 501–523.

Fontes, R.L.S., & Cox, F.R. 1998. Zinc toxicity in soybean grown at high iron concentration in nutrient solution. Journal of Plant Nutrition, 21, 1723–1730.

Franks, D.M., Boger, D.V., Côte, C.M., & Mulligan, D.R. 2011. Sustainable development principles for the disposal of mining and mineral processing wastes. Resource Policy, 36, 114–122.

Fraser Institute. 2012. How are waste materials managed at mine sites?

García-Esquinas, E., Pollán, M., Umans, J.G., Francesconi, K.A., Goessler, W., Guallar, E., Howard, B., Farley, J., Best, L.G., & Navas-Acien, A. 2013. Arsenic exposure and cancer mortality in a US-based prospective cohort: the strong heart study. Cancer Epidemiology, Biomarkers & Prevention, 22 (11), 1944-1953.

Ghani, A. 2010. Toxic effects of heavy metals on plant growth and metal accumulation in maize (Zea mays L.). Iranian Journal of Toxicology, 3 (3), 325–334.

Gibb, H., & O'Leary, K.G. 2014. Mercury exposure and health impacts among individuals in the artisanal and small-scale gold mining community: A comprehensive review. Environmental Health Perspectives, 122, 667–672.

Gibb, H.J., Lees, P.S.J., Pinsky, P.F., & Rooney, B.C. 2000. Lung cancer among workers in chromium chemical production. American Journal of Industrial Medicine, 38 (2), 115–126.

Gil, F., Facio, A., Villanueva, E., Perez, M.L., Tojo, R., & Gil, A. 1996. The Association of tooth lead content with dental health factors. The Science of the Total Environment, 192 (2), 183.

Hamada, A.J., Esteves, S.C., & Agarwal, A. 2013. A comprehensive review of genetics and genetic testing in azoospermia. Clinics (Sao Paulo), 68 (1), 39-60.

Harish, E., & David, M. 2015. Assessment of potentially toxic cyanide from the gold and copper mine ore tailings of Karnataka, India. International Journal of Science and Technology, 3, 171–178.

He, Z.L., Yang, X.E., Stoffella, P.J. 2005. Trace elements in agroecosystems and impacts on the environment. Journal of Trace Elements Medical Biology, 19(2–3), 125–140.

Heck, J.E., Park, A.S., Qiu, J., Cockburn, M., & Ritz, B. 2014. Risk of leukemia in relation to exposure to ambient air toxics in pregnancy and early childhood. International Journal of Hygiene and Environmental Health, 217 (6), 662-668.

Hegedus, A., Erdei, S., & Horvath, G. 2001. Comparative studies of H2O2 detoxifying enzymes in green and greening barley seedings under cadmium stress. Plant Science, 160, 1085–

1093.

Hopenhayn, C., Huang, B., Christian, J., Peralta, C., Ferreccio, C., Atallah, R., & Kalman, D. 2003. Profile of urinary arsenic metabolites during pregnancy. Environmental Health Perspective, 111 (16), 1888-1891.

Hussain, A., Abbas, N., Arshad, F., et al. 2013. Effects of diverse doses of lead (Pb) on different growth attributes of Zea mays L. Agricultural Sciences, 4 (5), 262–265.

International Institute for Environment and Development (IIED). 2002. Mining for the future – Appendix A: Large volume waste working paper.

Israr, M., Sahi, S., Datta, R., & Sarkar, D. 2006. Bioaccumulation and physiological effects of mercury in Sesbania drummonii. Chemosphere, 65, 591–598.

Jakubick, A.T., McKenna, G., & Robertson, A. MacG. 2003. Stabilisation of tailings deposits: International experience. In: Proceedings of Mining and the Environment III, Sudbury, Ontario, Canada, 25-28 May.

Jan, A.T., Ali, A., & Haq, Q.M.R. 2011. Glutathione as an antioxidant in inorganic mercury induced nephrotoxicity. Journal of Postgraduate Medicine, 57, 72–77.

Jayakumar, K., Rajesh, M., Baskaran, L., & Vijayarengan, P. 2013. Changes in nutritional metabolism of tomato (Lycopersicon esculantum Mill.) plants exposed to increasing concentration of cobalt chloride. International Journal of Food Nutrition and Safety, 4 (2), 62–69.

Jayakumar, K., Jaleel, C.A., & Azooz, M.M. 2008. Phytochemical changes in green gram (Vigna radiata) under cobalt stress. Global Journal of Molecular Sciences, 3 (2), 46–49.

Jayakumar, K., Jaleel, C.A., & Vijayarengan, P. 2007. Changes in growth, biochemical constituents, and antioxidant potentials in radish (Raphanus sativus L.) under cobalt stress. Turkish Journal of Biology, 31 (3), 127–136.

Jiang, H., Li, T., Han, X., Yang, X., & He, Z. L. 2012. Effects of pH and low molecular weight organic acids on competitive adsorption and desorption of cadmium and lead in paddy soils. Environmental Monitoring and Assessment, 184, 6325–6335.

Jiang, Y.M., Mo, X.A., Du, F.Q., Fu, X., Zhu, X.Y., Gao, H.Y., Xie, J.L., Liao, F.L., Pira, E., & Zheng, W. 2006. Effective treatment of manganese-induced occupational Parkinsonism with p-aminosalicylic acid: a case of 17-year follow-up study. Journal of Occupational and Environmental Medicine, 48 (6), 644–649.

Jiang, Y., & Zheng, W. 2005. Cardiovascular toxicities upon manganese exposure. Cardiovascular Toxicology, 5 (4), 345-354.

Jiang, W., Liu, D., & Hou, W. 2001. Hyperaccumulation of cadmium by roots, bulbs and shoots of garlic. Bioresource Technology, 76 (1), 9–13.

Jin, T., Nordberg, M., Frech, W., Dumont, X., Bernard, A., Ye, T.T., Kong, Q., Wang, Z., Li, P., Lundström, N.G., Li, Y., & Nordberg, G.F. 2002. Cadmium biomonitoring and renal dysfunction among a population environmentally exposed to cadmium from smelting in China (ChinaCad). Biometals, 15 (4), 397-410.

Johansson, S., Svensson, H., & Denekamp, J. 2000. Timescale of evolution of late radiation injury after postoperative radiotherapy of breast cancer patients. International Journal of Radiation Oncology, Biology, Physics, 48, 745-750.

Jorgensen, P.J., Dahl, R., Grandjean, P., Wahl, P., White, R.F., & Sorensen, N. 1997. Cognitive Deficit in 7-Year-Old Children with Prenatal Exposure to Methylmercury. Neurotoxicology and Teratology, 19 (6), 417-428.

Kabir, M., Iqbal, M.Z., & Shafiq, M. 2009. Effects of lead on seedling growth of Thespesia populnea L. Advances in Environmental Biology, 3 (2), 184–190.

Kale, H. 1993. Response of roots of trees to heavy metals. Environmental and Experimental Botany, 33, 99-119.

Kamal, M., Ghalya, A.E., Mahmouda, N., & Cote, R. 2004. Phytoaccumulation of heavy metals by aquatic plants. Environ. Intern., 29, 1029–1039.

Kandeler, E., Lurienegger, G., & Schwarz, S. 1997. Influence of heavy metals on the functional diversity of soil microbial communities. Biology and Fertility of Soils, 23, 299-306.

Khalid, B.Y., & Tinsley, J. 1980. Some effects of nickel toxicity on rye grass. Plant and Soil, 55 (1), 139–144.

Kjaer, C., & Elmegaard, N. 1996. Effects of copper sulphate on black bindweed (Polygonum convolvulus L.). Ecotoxicology and Environmental Safety, 33 (2), 110–117.

Kodama, H., Fujisawa, C., & Bhadhprasit, W. 2012. Inherited Copper Transport Disorders: Biochemical Mechanisms, Diagnosis, and Treatment. Current Drug Metabolism, 13 (3), 237–250.

Kumar, R., Gupta, A.K., Chattree, A., & Tripathi, R.M. 2013. A Review on the detection of heavy metals in water bodies, fish organs, sediment riverbeds., International Journal of Current Research and Reviews, 5 (18), 41-46.

Lee, M.Y., Bae, O.N., Chung, S.M., Kang, K.T., Lee, J.Y., & Chung, J.H. 2002. Enhancement of platelet aggregation and thrombus formation by arsenic in drinking water: a contributing factor to cardiovascular disease. Toxicology and Applied Pharmacology, 179 (2), 83-88.

Lee, D.H., Zo, Y.G., & Kim, S.J. 1996. Non-radioactive methods to study genetic Profiles of natural bacterial communities by PCR-single-strand-conformation polymorphism. Applied and Environmental Microbiology, 62 (9), 3112-3120.

Lewis, S., Donkin, M.E., & Depledge, M.H. 2001. Hsp 70 expression in Enteromorpha intestinalis (Chlorophyta) exposed to environmental stressors. Aquatic Toxicology, 51, 277–291.

Leyssens, L., Vinck, B., Van Der Straeten, C., Wuyts, F., & Maes, L. 2017. Cobalt toxicity in humans - A review of the potential sources and systemic health effects. Toxicology, 387, 43-56.

Lim, H.W., Collins, S.A.B., Resneck, J.S. Jr., Bolognia, J.L., Hodge, J.A., Rohrer, T.A., et al. 2017. The burden of skin disease in the United States. Journal of the American Academy of Dermatology, 76 (5), 958–972.

Lin, H.J., Sung, T.I., Chen, C.Y., & Guo, H.R. 2013. Arsenic levels in drinking water and mortality of liver cancer in Taiwan. Journal of Hazardous Materials, 262, 1132-1138.

Lin, Y.C., & Kao, C.H. 2005. Nickel toxicity of rice seedlings: Cell wall peroxidase, lignin, and $NiSO_4$-inhibited root growth. Crop, Environment Bioinformatics, 2, 131–136.

Mahurpawar, M. 2015. Effects of Heavy metals on Human health. International Journal of Research – GRANTHAALAYAH, Social Issues and Environmental Problems, 1 -7.

Manivasagaperumal, R., Balamurugan, S., Thiyagarajan, G., & Sekar, J. 2011. Effect of zinc on germination, seedling growth and biochemical content of cluster bean (Cyamopsis tetragonoloba (L.) Taub). Current Botany, 2 (5), 11–15.

Marin, A.R., Pezeshki, S.R., Masscheleyn, P.H., & Choi, H.S. 1993. Effect of dimethylarsinic acid (DMAA) on growth, tissue arsenic and photosynthesis of rice plants. Journal of Plant Nutrition, 16 (5), 865–880.

Martin, S., & Griswold, W. 2009. Human health effects of heavy metals. Environmental Science and Technology Briefs for Citizens, 15, 1–6.

Masindi, V., & Muedi, K.L. 2018. Environmental Contamination by Heavy Metals, Heavy Metals, Hosam El-Din M. Saleh and Refaat F. Aglan, IntechOpen, DOI: 10.5772/intechopen.76082.

Masters, R. 1998. Environmental Pollution, Neurotoxicity and Criminal Violence. International Journal of Environmental Toxicology, Rose (ed). Gordon and Breach: London.

Maya, M., Musekiwa, C., Mthembi, P., & Crowley, M. 2015. Remote sensing and geochemistry techniques for the assessment of coal mining pollution, Emalahleni (Witbank), Mpumalanga. South African Journal of Geomatics, 4 (2), 174–188.

Meeker, J.D., Rossano, M.G., Protas, B., et al. 2010. Environmental exposure to metals and male reproductive hormones: circulating testosterone is inversely associated with blood molybdenum. Fertility and Sterility, 93 (1), 130–140.

Meharg, A.A. 2004. Arsenic in rice – understanding a new disaster for south-east Asia. Trends in Plant Science, 9, 415–417.

Meliker, J.R., Slotnick, M.J., AvRuskin, G.A., Schottenfeld, D., Jacquez, G.M., Wilson, M.L., Goovaerts, P., Franzblau, A., & Nriagu, J.O. 2010. Lifetime exposure to arsenic in drinking water and bladder cancer: a population-based case-control study in Michigan, USA. Cancer Causes Control, 21 (5), 745-757.

Messer, R.L., Lockwood, P.E., Tseng, W.Y., Edwards, K., Shaw, M., Caughman, G.B., Lewis, J.B., & Wataha, J.C. 2005. Mercury (II) alters mitochondrial activity of monocytes at sublethal doses via oxidative stress mechanisms. Journal of Biomedical Materials Research - Part B – Applied Biomaterial, 75, 257–263.

Misra, S.G., & Mani, D. 1991. Soil pollution. Ashish Publishing House, Punjabi Bagh.

Mitileni, C., Gumbo, J., Muzerengi, C., & Dacosta, F. 2011. The distribution of toxic metals in sediments: Case study of new union gold mine tailings, Limpopo, South Africa. In Mine Water—Managing the Challenges; IMWA: Aachen, Germany.

Moral, R., Gomez, I., Pedreno, J.N., & Mataix, J. 1996. Absorption of Cr and effects on micronutrient content in tomato plant (Lycopersicum esculentum M.). Agrochimica, 40 (2-3), 132–138.

Moral, R., Pedreno, J.N., Gomez, I., & Mataix, J. 1995. Effects of chromium on the nutrient element content and morphology of tomato. Journal of Plant Nutrition, 18 (4), 815–822.

Moustakas, M., Lanaras, T., Symeonidis, L., & Karataglis, S. 1994. Growth and some photosynthetic characteristics of field grown Avena sative under copper and lead stress. Photosynthetica, 30 (3), 389–396.

Nagajyoti, K.P.C., Lee, K.D., & Sreekanth, T.V.M. 2010. Heavy metals, occurrence and toxicity for plants: a review. Environmental Chemistry Letters, 8 (3), 199-216.

Ndlovu, S., Simate, G.S., & Matinde, E. 2017. Waste production and utilization in the metal extraction industry. Print ISBN: 9781498767293.

Neelima, P., & Reddy, K.J. 2002. Interaction of copper and cadmium with seedlings growth and biochemical responses in Solanum melongena. Environmental Pollution and Technology, 1, 285–290.

Nematshahi, N., Lahouti, M., & Ganjeali A. 2012. Accumulation of chromium and its effect on growth of (Allium cepa cv. Hybrid)," European Journal of Experimental Biology, 2 (4), 969–974.

Nizam, S., Kato, M., Yatsuya, H., Khalequzzaman, M., Ohnuma, S., Naito, H., & Nakajima, T. 2013. Differences in urinary arsenic metabolites between diabetic and non-diabetic subjects in Bangladesh. International Journal of Environmental Research and Public

Health, 10 (3), 1006-1019.

Nogawa, K., Kobayashi, E., Okubo, Y., & Suwazono, Y. 2004. Environmental cadmium exposure, adverse effects and preventive measures in Japan. Biometals, 17 (5), 581-587.

Nordberg, G.F. 2004. Cadmium and health in the 21st century- historical remarks and trends for the future, 17 (5), 485-489.

Okereafor, G., Makhatha, M., Mekuto, L., & Mavumengwana, V. 2019. Evaluation of trace elemental levels as pollution indicators in an abandoned gold mine dump in Ekuhurleni area, South Africa. In: Trace Elements in the Environment – New Approaches and Recent Advances. IntechOpen, ISBN: 978-1-83880-332-2.

Okereafor, G.U., Mulaba-Bafubiandi, A.F., & Mavumengwana, V. 2017. Possible heavy metals transportation and ground erosion during heavy rainfall in rural Mangweni (Tzaneen, Limpopo Province, South Africa). The South African Institute of Mining and Metallurgy, 515–522.

Ouzounidou, G. 1994. Change in chlorophyll fluorescence as a result of copper treatment: dose response relations in Silene and Thlaspi. Photosynthetica., 29, 455–462.

Panda, S.K., & Patra, H.K. 2000. Nitrate and ammonium ions effect on the chromium toxicity in developing wheat seedlings. Proceedings of the National Academy of Sciences, India, 70, 75–80.

Pandolfini, T., Gabbrielli, R., & Comparini, C. 1992. Nickel toxicity and peroxidase activity in seedlings of Triticum aestivum L. Plant, Cell and Environment, 15 (6), 719–725.

Percival, H.J., Speir, T.W., & Parshotam, A. 1999. Soil solution chemistry of contrasting soils amended with heavy metals. Australian Journal of Soil Research, 37 (5), 993–1004.

Plum, L.M., Rink, L., & Haase, H. 2010. The essential toxin: impact of zinc on human health.

International Journal of Environmental Research and Public Health, 7 (4), 1342–1365.

Prasad, K.V.S.K., Pardha saradhi, P., & Sharmila, P. 1999. Concerted action of antioxidant enzyme and curtailed growth under zinc toxicity in Brassica juncea. Environmental and Experimental Botany, 42, 1–10.

Qin, T.C., Wu, Y.S., & Wang, H.X. 1994. Effect of cadmium, lead and their interactions on the physiological and biochemical characteristics of Brassica chinensis. Acta Ecologica Sinica, 14 (1), 46-49.

Rafiei, B., Bakhtiari Nejad, M., Hashemi, M., & Khodaei, A. 2010. Distribution of heavy metals around the Dashkasan Au mine. International Journal of Environmental Research, 4, 647–654.

Raj, B.G., Patnaik, M.C., Babu, S.P., Kalakumare, B., Singh, M.V., & Shylaja, J. 2006. Heavy metal contaminants in water-soil-plant-animal continuum due to pollution of Musi river around Hyderabad in India. Indian Journal of Animal Science, 76, 131-133.

Rajaganapathy, V., Xavier, F., Sreekumar, D., & Mandal, P.K. 2011. Heavy metal contamination in soil, water and fodder and their presence in livestock and products: A Review. Journal of Environmental Science and Technology, 4 (3), 234-249.

Ray, R.R. 2016. Adverse hematological effects of hexavalent chromium: an overview. Interdisciplinary Toxicology, 9 (2), 55-65.

Reddy, A.M., Kumar, S.G., Jyotsnakumari, G., Thimmanayak, S., & Sudhakar, C. 2005. Lead induced changes in antioxidant metabolism of horsegram (Macrotyloma uniflorum (Lam.) Verdc.) and bengalgram (Cicer arietinum L.). Chemosphere, 60, 97–104.

Rendall, R.E.G., Phillips, J.I., & Renton, K.A. 1994. Death following exposure to fine particulate nickel from a metal arc process, Annals of Occupational Hygiene, 38, 921-930.

Rice, K.M., Walker, E.M. Jr., Wu, M., Gillette, C., & Blough, E.R. 2014. Environmental mercury and its toxic effects. J. Prev. Med. Public Health, 47 (2), 74–83.

Ritcey, G.M. 1989. Tailings management: Problems and solutions in the mining industry. Elsevier, New York.

Robert, L., & Jones, P.D. 2009. Blood lead levels and blood lead the change tendency of the test in the United States from 1998 to 2004. Pediatrics, 4 (8), 502-514.

Ross, A.C., Taylor, C.L., Yaktine, A.L., et al. 2011. Overview of Calcium. Dietary Reference Intakes for Calcium and Vitamin D. Institute of Medicine (US) Committee on Review Dietary Reference Intakes for Vitamin D and Calcium, Washington (DC): National Academies Press (US).

Rossman, T.G., Uddin, A.N., & Burns, F.J. 2004. Evidence that arsenite acts as a cocarcinogen in skin cancer. Review. Toxicology and Applied Pharmacology, 198 (3), 394-404.

SANS. 1998. Code of Practice for Mine Residue Deposits., South African Bureau of Standards. ISBN: 0626117003. 129.

Santanu, B., & Chumki, B. 2018. The impact of heavy metal contamination on soil health. In: Reicosky, D. (ed.), Managing soil health for sustainable agriculture Volume 2: Monitoring and management, Burleigh Dodds Science Publishing, Cambridge, UK, ISBN: 9781786761927.

Seidal, K., Jörgensen, N., Elinder, C.G., Sjögren, B., & Vahter, M. 1993. Fatal cadmium-induced pneumonitis. Scandinavian Journal of Work, Environment & Health, 19 (6), 429-431.

Sharma, P., & Dubey, R.S. 2005. Lead toxicity in plants. Brazilian Journal of Plant Physiology, 17, 35–52.

Sharma, O.P., Rajesh Jain, K.S., & Sharma, P.K. 2004. Heavy metals accumulation in soils irrigated by municipal and industrial effluent. Journal of Environmental Science and Engineering, 46, 65-73.

Sharma, D.C., & Sharma, C.P. 1993. Chromium uptake and its effects on growth and biological yield of wheat. Cereal Research Communications, 21 (4), 317–322.

Sheikh, I. 2016. Cobalt Poisoning: A Comprehensive Review of the Literature. Journal of Medical Toxicology and Clinical Forensic Medicine, 2 (2.5), 1–6.

Shekar, C.H.C., Sammaiah, D., Shasthree, T., & Reddy, K.J. 2011. Effect of mercury on tomato growth and yield attributes. International Journal of Pharmacology and Biological Sciences, 2 (2), 358–364.

Sheldon, A.R., & Menzies, N.W. 2005. The effect of copper toxicity on the growth and root morphology of Rhodes grass (Chloris gayana Knuth.) in resin buffered solution culture. Plant and Soil, 278 (1-2), 341–349.

Shenker, M., Plessner, O.E., & Tel-Or, E. 2004. Manganese nutrition effects on tomato growth, chlorophyll concentration, and superoxide dismutase activity. Journal of Plant Physiology, 161 (2), 197–202.

Sheoran, I.S., Singal, H.R., & Singh, R. 1990. Effect of cadmium and nickel on photosynthesis and the enzymes of the photosynthetic carbon reduction cycle in pigeonpea (Cajanus cajan L.). Photosynthesis Research, 23 (3), 345–351.

Smith, A.H., Marshall, G., Yuan, Y., Ferreccio, C., Liaw, J., von Ehrenstein, O., Steinmaus, C., Bates, M.N., Selvin, S. 2006. Increased mortality from lung cancer and bronchiectasis in young adults after exposure to arsenic in utero and in early childhood. Environmental Health Perspective, 114 (8), 1293-1296.

Sobha, K., Poornima, A., Harini, P., & Veeraiah, K. 2007. A study on biochemical changes in the freshwater fish, catla catla (Hamilton) exposed to the heavy metal toxicant cadmium chloride. Kathmandu University Journal of Science, Engineering and Technology, 1 (4), 1–11.

Soliman, Z.I. 2006. A study of Heavy Metals Pollution in some Aquatic Organisms in Suez Canal in Port-Said Harbour. Journal of Applied Sciences Research, 2 (10), 657–663.

Souza, T.S., Christofoletti, C.A., Bozzatto, V., Fontanetti, C.S. 2014. The use of diplopods in soil ecotoxicology—A review. Ecotoxicology and Environmental Safety, 103, 68-73

Spangler, A.H., & Spangler, J.G. 2009. Groundwater manganese and infant mortality rate by county in North Carolina: an ecological analysis. Ecohealth, 6 (4), 596-600.

Speira, T. W., Kettlesb, H. A., Percivalc, H. J., & Parshotam, A. 1999. Is soil acidification the cause of biochemical responses when soils are amended with heavy metal salts? Soil Biology and Biochemistry, 31, 1953–1961.

Sträter, E., Westbeld, A., Klemm, O. 2010. Pollution in coastal fog at Alto Patache, Northern Chile. Environmental Science Pollut Res Int.

Sudhakar, C., Symalabai, L., & Veeranjaveyuler, K. 1992. Lead tolerance of certain legume species grown on lead or tailing. Agriculture, Ecosystems and Environment, 41, 253–261.

Sunderman, F.W., Dingle, B., Hopfer, S.M., & Swift, T. 1988. Acute nickel toxicity in electroplating workers who accidentally ingested a solution of nickel sulphate and nickel chloride. American Journal of Industrial Medicine, 14, 257-266.

Taweel, A., Shuhaimi-Othman, M., & Ahmad, A.K. 2011. Heavy metals concentration in different organs of tilapia fish (Oreochromis niloticus) from selected areas of Bangi, Selangor, Malaysia. African Journal of Biotechnology, 10, 11562-11566.

Teo, J., Goh, K., Ahuja, A., Ng, H., & Poon, W. 1997. Intracranial vascular calcifications, glioblastoma multiforme, and lead poisoning. American Journal of Neuroradiology,18, 576–579.

Teresa, M., Vasconcelos, S.D., & Tavares, H.M. 1997. Trace element concentrations in blood and hair of young apprentices of a technical-professional school. Science of the Total Environment, 205, 189-199.

Thomas, F., Malick, C., Endreszl, E.C., & Davies, K.S. 1998. Distinct responses to copper stress in the halophyte, Mesembryan-themum crystallium. Physiologia Plantarum, 102, 360–368.

Tsai, S.Y., Chou, H.Y., The, H.W., Chen, C.M., & Chen, C.J. 2003. The effects of chronic arsenic exposure from drinking water on the neurobehavioral development in adolescence. Neurotoxicology, 24 (4-5), 747-753.

Van Assche, F., & Clijsters, H. 1990. Effects of metals on enzyme activity in plants. Plant Cell Environment, 13 (3), 195–206.

Vega, F.A., Covelo, E.F., & Andrade, M. 2006. Competitive sorption and desorption of heavy metals in mine soils: Influence of mine soil characteristics. Journal of Colloid and Interface Science, 298, 582–592.

Vega, F., Covelo, E., Andrade, M., & Marcet, P. 2004. Relationships between heavy metals content and soil properties in mine soils. Analytica Chimica Acta, 524, 141–150.

Vick, S.G. 1990. Planning, design, and analysis of tailings dams. Vancouver, BiTech. Publishers Ltd. 2nd Edition. 369, ISBN: 0921095120.

Vieira, C., Morais, S., Ramos, S., Delerue-Matos, C., & Oliveira, M.B.P.P. 2011. Mercury, cadmium, lead and arsenic levels in three pelagic fish species from the Atlantic Ocean:

intra- and inter-specific variability and human health risks for consumption. Food & Chemical Toxicology, 49, 923-932.

Vousta, D., Gramanis, A., & Samara, C. 1996. Trace elements in vegetables grown in an industrial area in relation to soil and air particulate matter. Environmental Pollution, 94, 325-335.

Wang, Q.Y., Sun, J.Y., Xu, X.J., Yu, H.W. 2018. Integration of chemical and toxicological tools to assess the bioavailability of copper derived from different copper-based fungicides in soil. Ecotoxicology and Environmental Safety, 161, 662-668.

Wang, W., Zou, J., Duan, X., Jiang, W., & Liu, D. 2007. Cadmium accumulation and its effects on metal uptake in maize (Zea mays L.). Bioresource Technology, 98 (1), 82–88.

Wang, Y., & Greger, M. 2004. Clonal differences in mercury tolerance, accumulation, and distribution in willow. Journal of Environmental Quality, 33, 1779–1785.

Wasserman, G.A., Liu, X., Parvez, F., Ahsan, H., Factor-Litvak, P., van Geen, A., Slavkovich, V., LoIacono, N.J., Cheng, Z., Hussain, I., Momotaj, H., & Graziano, J.H. 2004. Water arsenic exposure and children's intellectual function in Araihazar, Bangladesh. Environmental Health Perspective, 112 (13), 1329-1333.

Woo, S., Yum, S., Park, H.S., Lee, T.K., & Ryu, J.C. 2009. Effects of heavy metals on antioxidants and stress-responsive gene expression in Javanese medaka (Oryzias javanicus). Comparative Biochemistry and Physiology, Part C, 149, 289–299.

Wood, J.M. 1974. Biological cycles for toxic elements in the environment. Science, 183, 1049-1052.

World Health Organization (WHO). 1995. Guidelines for Drinking Water Quality. World Health Organization, Geneva, Switzerland, 121.

Xie, Y., Fan, J., Zhu, W., Amombo, E., Lou, Y., Chen, L., & Fu, J. 2016. Effect of heavy metals pollution on soil microbial diversity and Bermudagrass genetic variation. Frontiers in Plant Science, 7, 755.

Xie, X., Zhu, W., Liu, N., & Liu, J. 2013. Bacterial community composition in reclaimed and unreclaimed tailings of Dexing copper mine, China. African Journal of Biotechnology, 12, 4841–4849.

Yabe, J., Ishizuka, M., et al. 2010. Current Levels of Heavy metal contamination in Africa. Journal of Veterinary Medical Science, 72 (10), 1257-1263.

Yao, J., Tian, L., Wang, Y., Djah, A., Wang, F., Chen, H., Su, C., Zhuang, R., Zhou, Y., Choi, M.M.F., et al. 2008. Microcalorimetric study the toxic effect of hexavalent chromium on microbial activity of Wuhan brown sandy soil: An in vitro approach. Ecotoxicology and Environmental Safety, 69, 89–95.

Yourtchi, M.S., & Bayat, H.R. 2013. Effect of cadmium toxicity on growth, cadmium accumulation and macronutrient content of durum wheat (Dena CV.). International Journal of Agriculture and Crop Sciences, 6 (15), 1099–1103.

Yu, L., Yan-bin, W., Xin, G., Yi-bing, S., & Gang, W. 2006. Risk assessment of heavy metals in soils and vegetables around non-ferrous metals mining and smelting sites, Baiyin, China Journal of Environmental Science, 18 (6), 1124–1134.

Yusuf, M., Fariduddin, Q., Varshney, P., & Ahmad, A. 2012. Salicylic acid minimizes nickel and/or salinity-induced toxicity in Indian mustard (Brassica juncea) through an improved antioxidant system. Environmental Science and Pollution Research, 19, 8–18.

Zdrojewicz, Z., Popowicz, E., & Winiarski, J. 2016. Nickel - role in human organism and toxic effects. Pol. Merkur. Lekarski.; 41 (242), 115-118.

Zhang, Z.J., Lu, Q.F., & Fang, F. 1989., Effect of Mercury on the growth and physiological function of wheat seedlings. Chinese Journal of Environmental Science, 10 (4), l0-13.

Zhang, W.H., & Tyerman, S.D. 1999. Inhibition of water channels by HgCl2 in intact wheat root cells. Plant Physiology, 120, 849–857.

Zhou, Z.S., Huang, S.Q., Guo, K., Mehta, S.K., Zhang, P.C., & Yang, Z.M. 2007. Metabolic adaptations to mercury-induced oxidative stress in roots of Medicago sativa L. Journal of Inorganic Biochemistry, 101, 1–9.

CHAPTER 3

RESULTS

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Evaluation of trace elemental levels as pollution indicators in an abandoned gold mine dump in Ekuhurleni area, South Africa.

3.0 Abstract.

In the Blesbokspruit area of Ekuhurleni, South Africa, previous gold mining activities resulted in many tailings being dumped for over two decades regardless of their danger to the environment. 20 representative soil samples were used in describing the prevalence such as manganese (Mn), nickel (Ni), arsenic (As), cadmium (Cd), cobalt (Co), copper (Cu), chromium (Cr), lead (Pb), and zinc (Zn). The soils were very strongly acidic ranging from 3.86 to 4.34 with a low cation exchange capacity (CEC). Based on X-ray fluorescence (XRF) analysis, elemental composition of the soils revealed average values of trace element oxides such as Na_2O (0.18 %), MgO (0.63 %), Al_2O_3 (6.51 %), SiO_2 (81.83 %), P_2O_5 (0.04 %), SO_3 (3.40 %), K_2O (1.98 %), CaO (0.45 %), TiO_2 (0.51 %), Cr_2O_3 (0.17 %), MnO (0.04 %), Fe_2O_3 (3.59 %), NiO (0.04 %), As_2O_3 (0.02 %), with Rb_2O and SrO falling below 0.01 %. Trace metals (TM) contamination levels in the soils were evaluated using various pollution indices such as contamination factor, degree of contamination, geo-accumulation index, pollution load index and the United States Environmental Protection Agency benchmarks for trace metals concentration in soil. The average concentration of various trace metals were 861.5 mg/kg for Cr; 326.8 mg/kg for Al; 202.2 mg/kg for As; 134.3 mg/kg for Fe; 123.7 mg/kg for Pb; 28.8 mg/kg for Co; 25.4 mg/kg for Ni; 8.5 mg/kg for Ti; 8.3 mg/kg for Cd; 4.5 mg/kg for Zn and 0.2 mg/kg for Cu. A very high degree of contamination and a polluted status were observed on account of the average contamination factor and polluted load index of the trace metals respectively.

Key words: Mine tailings, Trace metal, Pollution, Contamination factor, Geoaccumulation index.

3.1 Introduction.

South Africa like other developing countries is faced with the challenges of environmental degradation via the continuous release into the environment of trace element-containing chemicals through urbanization, agricultural and mining activities, as well as industrialization. Trace metals (TM) are naturally occurring elements that have a high atomic weight and a density at least 5 times greater than that of water, and some of the commonly found ones particularly at contaminated sites include Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Mercury (Hg), Nickel (Ni) and Zinc (Zn) (Akoto *et al*., 2008; Wuana & Okieimen, 2011). Attempts towards the assessment, mechanism and the characteristics of trace metal pollution in surrounding areas of mines has been and continue being a theme of various scientific gatherings.

Globally, the extraction and distribution of minerals from ore deposits has been one of the actions that contribute to environmental degradation due to industrialization. The extraction and beneficiation processes often result in the release of tailings that end up in natural percolations within the earth crust, thus paving a way for various kinds of risk elements entering the ecosystem. Such practices result in serious environmental complications due to the elevated concentrations and accumulation of trace metals which poses risk for human health (Sharma *et al*., 2007; Figueroa *et al*., 2010; Muhammad *et al*., 2011; Barbieri, 2016; Barkouch *et al*., 2016).

The mining and processing of gold is associated with certain elements such as Copper (Cu), Antimony (Sb), Nickel (Ni), Selenium (Se), Mercury (Hg), Thallium (Tl), Titanium (Ti), Zinc (Zn), Silver (Ag), Cobalt (Co), Lead (Pb) and Uranium (U). Most of these metals are somewhat released into the environment via trophic links ranging from agricultural soils to plants, animals and humans (Loureiro *et al*., 2005; Mann *et al*., 2011; Landers, 2016).

Pollutants from various anthropogenic activities ranging from mine effluents such as wastewaters, tailings, runoff from agricultural pesticides and atmospheric deposition often contaminate the surrounding soils and water bodies thus posing threat to the ecosystem and humans. This occurs via direct ingestion or contact with contaminated soil, the food chain (soil-plant-human or soil-plant-animal-human), drinking of contaminated ground water, reduction in food quality (safety and marketability) via phytoxicity, reduction in land usability for agricultural production causing food insecurity, and land tenure problems (McLaughlin *et al*., 2000; Song *et al*., 2010). In humans, several health challenges such as abortion, cancer, kidney damage and sometimes death, are some of the consequences of prolonged exposure to extreme concentrations of trace metals (Okereafor *et al.*, 2018).

The importance of soil cannot be over emphasized as it is characterized as a complex and dynamic system that is made up of sediments that are different in relation to their physical, chemical, mineralogical and biological constituents. Soil is an essential resource for natural living conditions of plants, animals and humans. The role of soil as a collector filter of both organic and inorganic residues helps in protecting groundwater and in the sequestration of toxic materials (BIO, 2014). The accumulation of excess metals and metalloids in soils over an extended period exposes humans and other animals to toxicity (Shafie *et al*., 2013). Assessing the spatial distribution of trace metals in soil is crucial to obtaining basic information about areas of concerns and to prioritize site mitigation strategies (Xiao-san *et al*., 2011). However, the quantification of element concentrations in soil as a single parameter is not enough in evaluating the extent of contamination due to differentiation between natural background levels and anthropogenic enrichment (Barbieri, 2016). Indexes including Geoaccumulation index (I_{geo}) and contamination factor (CF) which are known to provide a better picture of the status of elemental contamination compared to the background concentration were used as pointers in identifying and quantifying the level of elemental pollution as well as the intensity of anthropogenic contaminants accumulated in the soil.

There are enormous impacts of mine tailings disposal sites with over 500,000 abandoned hard rock mines located in the United States, while Mexico alone is affected by 27.1 million hectares of mining activity (USEPA, 2004; Schwegler, 2006; Ebenebe *et al*., 2017). Gold mine waste was reported in 2001 by South Africa's Department of Water Affairs and Forestry as the largest single source of waste constituting over 47% of mineral wastes generated in South Africa (Oelofse *et al*., 2007). Previous studies indicate that there are close to 300 unlined and not vegetated tailings dumps covering over 400 km^2 surface area within the Witwatersrand Basin of the Republic of South Africa. With tailings dumps being a major source of contaminants, the Witwatersrand Basin's massive tailing dumps are a possible, environmental pollution threat (AngloGold, 2004). Studies into the deposits in the mine regions of the Gauteng province of South Africa (Ebenebe *et al*., 2017), revealed the deposits to be of great health concern; containing enormous amounts of toxic metals, such as U, As, Ra, Ni, Zn, etc.

Hence, this present study was aimed at determining the contamination level of identified trace metals in an abandoned mine tailing dump over time. In addition, findings from this study will assist the various stakeholders in resource management and policy implementation.

3.2 Materials and methods.

3.2.1 Description of the study area.

South Africa lies in the southernmost part of the African continent, and is known to have a renowned varied topography, great natural beauty, and cultural diversity. It is a medium-sized country, with a total land area of 1,219,090 square kilometers. Ekurhuleni falls within the East Rand region and is characterized by rainfall known to be typical to the Highveld summer rainfall, which occurs from October to April. The average annual rainfall varies from 715 mm to 735 mm an indication that the study area has a distinct moisture deficit. Frost does occur frequently from mid-April to September, which makes temperatures below freezing common during winter times. This area is home to mild summers with temperatures seldom above 30 ºC. During spring and winter, northerly and north-westerly winds occur and during summer north-easterly to north-north-easterly winds occur (EMM, 2007).

There are many pans across the Ekurhuleni area. These pans cover a total area of 3,559 hectares within the Ekurhuleni Metropolitan Municipality area and are mostly seasonal. There are also a few lakes created by mines, which are used for recreational parks. Germiston Lake, Benoni Lake, and Boksburg Lake are the three main lakes used for recreational purposes within the Ekurhuleni Metropolitan Municipality area, but which fall outside the East Rand Basin area. The tailings dump has some informal settlements within its proximity with subsistence farming amongst the dwellers as shown in **Figure 3.1**. The specific description indicating coordinates of the sampling site located along Outeniqua Road & Cloverfield Weg in Springs, Ekurhuleni are illustrated in **Table 3.1**.

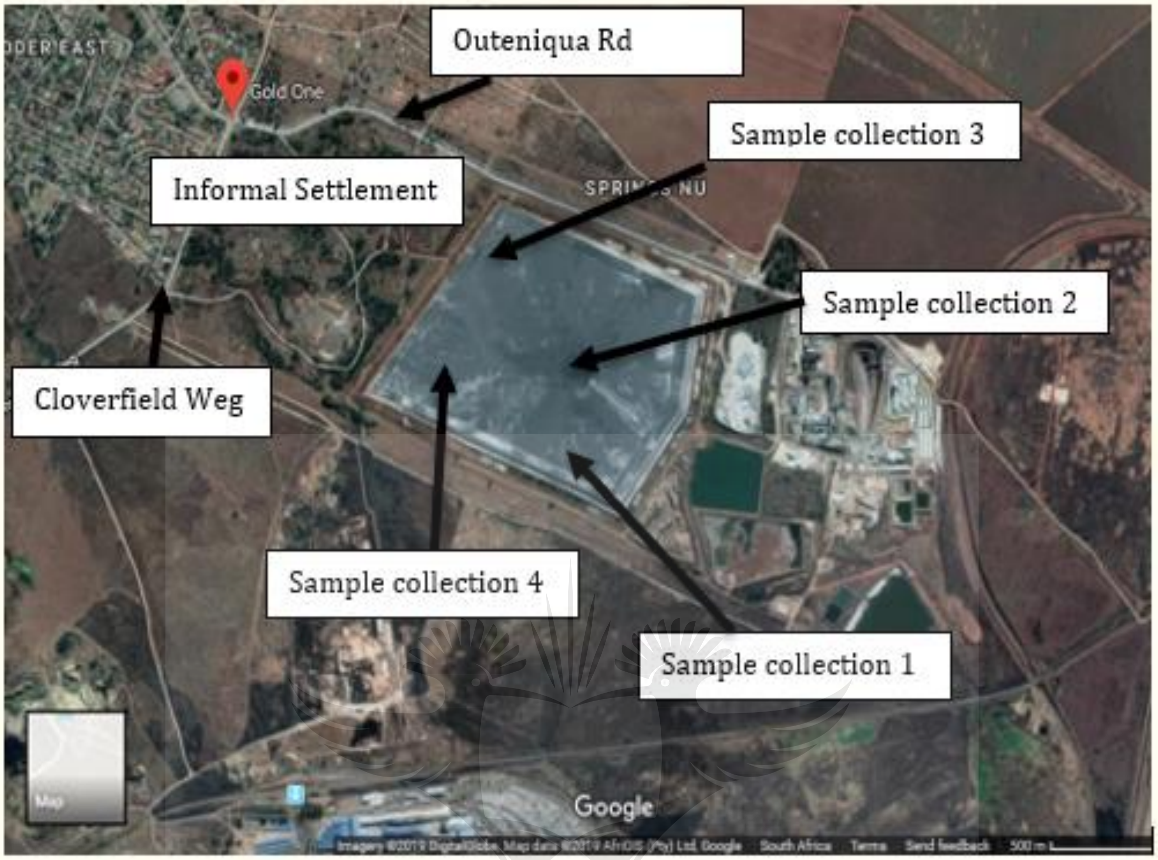

Figure 3. 1 Location of the sampling site

Table 3. 1 Location of the Blesbokspruit gold mine tailings sediment samples

Station No.	Latitude (S)	Longitude (E)
1	26^0 10′	28^0 27′
2	26^0 15′	28^0 35′
3	26^0 04′	28^0 40′
4	26^0 17′	28^0 44′
5	26^0 21′	28^0 50′
6	26^0 30′	29^0 10′
7	26^0 00′	29^0 15′
8	26^0 27′	29^0 20′
9	26^0 09′	29^0 35′
10	26^0 38′	29^0 42′
11	26^0 43′	29^0 47′
12	26^0 34′	29^0 50′
13	26^0 13′	29^0 53′
14	26^0 19′	30^0 10′
15	26^0 48′	30^0 15′
16	26^0 36′	30^0 25′
17	26^0 40′	30^0 29′
18	26^0 14′	30^0 35′
19	26^0 23′	30^0 40′
20	26^0 54′	30^0 48′

3.2.2 Sampling (material) description.

In a bid to assess the level of trace metal contamination in the mine tailings, about 2 kilograms of 20 representative tailing samples were obtained from the dump. Preceding the removal of top tailing samples (2 cm) using an auger, samples were taken at a depth of 10 cm for every 50 m horizontal interval for a wider coverage. The collected soil samples (tailings) were kept cool in an icebox (< 4 ^{o} C) and transported to the laboratory for further analyses in sterile plastic bags.

3.3 Analysis.

3.3.1 Experimental analysis.

Twenty (20) representative tailing samples of about 5 g each were oven dried at 100 ºC for 24 hours and passed through a 2 mm sieve. Aliquots of approximately 2 g of the various tailing samples were weighed into a Teflon crucible and moistened with 100 mL of 1M HCl acid for the determination of the HCl-soluble fraction of toxic metals. The mixtures were covered and placed on a shaker for 12 hours at 130 rpm. The solutions were filtered through a Whatmann filter paper, and the filtrates were stored in sterile bottles prior to analysis of minerals using inductively coupled plasma-optical emission spectrometry (ICP-OES).

Ten (10) g each of the representative tailing samples were pelletized using a mould at very high pressure and then placed in the sample compartment of the X-ray fluorescence spectrometer (XRF; Rigaku ZSX PrismusII). This was done to analyse the major and trace element oxides of the tailing samples.

Physicochemical properties such as pH and EC (electrical conductivity) of the soil samples (tailings) were measured in a slurry suspension (1:2.5, w/w) and a 1:5 tailings-to-water suspension using a Crison multimeter (model MM 41) respectively (Aris *et al*., 2014). Loss on Ignition (LOI) analysis was used to determine the organic matter content (% OM) of the various tailing's samples (Robertson, 2011). The grain size distribution of tailing samples was determined using the hydrometer method (ASTM, 2007).

3.3.2 Quality assurance and quality control.

Apparatus and glassware used were acid-washed with 5 % nitric acid for precision analysis while reagents were of analytical standard. The trace metals were determined using ICP-OES (Model - GBC Quantima Sequential) operated under specific conditions of 1300W RF power, 15 L min^{-1} plasma flow, 2.0 L min^{-1} auxiliary flow, 0.8 L min^{-1} nebulizer flow, 1.5 mL min^{-1} sample uptake rate. Multiple levels of calibration standard solutions prepared from a Certipur ICP multi-element standard (Merck KGaA) was used in the calibration of the ICP-OES. Metal determination was done using Axial view, while 2-point background correction and 3 replicates were employed in the measurement of analytical signal. The emission intensities were determined for the most sensitive lines free of spectral interference. By diluting the stock multi-elemental standard solution (1000 mg L^{-1}) in 0.5 % (v/v) nitric acid, the calibration standards were prepared. The calibration curves for all the studied elements were in the range of 0.01 to 1.0 mg L^{-1}.

3.4 Data analyses.

The history and degree of trace metal pollution in an environment can be ascertained from the surrounding sediments by comparing the pollutant metal concentration with an unpolluted reference material. The average shale concentration as an International standard reference for unpolluted sediment was utilized (Turekian & Wedepohl, 1961). This study applied pollution indices such as (i) metal contamination factor, (ii) contamination degree, (iii) index of geo-accumulation, and (iv) pollution load index to assess trace metal contamination.

3.4.1 Assessment according to Contamination Factor.

By calculating the ratio of the concentration of a specific trace metal in the study area and the concentration of the background concentration of the corresponding metal, the contamination factor was determined. **Table 3.2** shows the various terminologies in describing contamination factor class and level (Hakanson, 1980). CF is an effective tool for monitoring pollution over a period and for the respective metals was calculated using the equation as prescribed by (Tomlinson *et al*., 1980).

$$CF = \frac{(\,Mean\ metal\ concentration\ at\ contaminated\ site\ (Cm))}{(Level\ of\ pre\text{-}industrial\ concentration\ of\ individual\ metal\ (Cbackground))} \qquad (1)$$

Table 3. 2 Terminologies used to describe contamination factor (Hakanson, 1980).

CF	**Description**
CF < 1	Low contamination factor
1 ≤ CF < 3	Moderate contamination factor
3 ≤ CF < 6	Considerate contamination factor
CF ≥ 6	Very high contamination factor

3.4.2 Assessment according to Contamination degree.

Contamination degree (CD) refers to the sum of all the contamination factor (CF) values of a specific sampling site. It is a diagnostic tool aimed at providing a measure of the degree of overall contamination in surface layers in a sampling site or core. In this study, CD was assessed using Equation (2).

$$CD = \sum_{i=0}^{n} cf \qquad (2)$$

A list of terminologies as prescribed by (Ahdy & Khaled, 2009) used in describing the contamination degree of the site under investigation is summarized in **Table 3.3.**

Table 3. 3 Terminologies used to describe contamination degree for soil (Ahdy & Khaled, 2009).

CD	Description
CD < 6	Low contamination degree
6 ≤ CD < 12	Moderate contamination degree
12 ≤ CD < 24	Considerate contamination degree
CD ≥ 24	Very high contamination degree

3.4.3 Assessment according to Geo-accumulation Index.

To quantify the level of toxic metal contamination associated with the study site, the geo-accumulation index (I-geo) was adopted. The I_{geo} is an important method used for the interpretation of the quality of sediments in the sampling site (Nulin *et al.*, 2013). It is used to assess impacts due to anthropogenic activities and was determined using equation (3) as prescribed by (Muller, 1969).

$$I_{geo} = \log_2 \frac{Cn}{1.5Bn} \tag{3}$$

Where C_n is the measure of the metal concentration in the examined metal n in the sediment, Bn is the background concentration of the element (average shale concentration) or reference value of the metal n, and 1.5 is the correction factor due to the lithogenic effect that could result in variations in the background values for a given metal in the environment. **Table 3.4** shows seven grades (0 – 6) ranging from unpolluted to highly polluted in the geo-accumulation index scale as described by (Muller, 1969).

Table 3. 4 Classification for the geo-accumulation index (Igeo) (Muller, 1969).

I_{geo} Value	Class	Contamination Level
$I_{geo} \leq 0$	0	Uncontaminated
$0 < I_{geo} < 1$	1	Uncontaminated/moderately contaminated
$1 < I_{geo} < 2$	2	Moderately contaminated
$2 < I_{geo} < 3$	3	Moderately/strongly contaminated
$3 < I_{geo} < 4$	4	Strongly contaminated
$4 < I_{geo} < 5$	5	Strongly/extremely contaminated
$5 < I_{geo}$	6	Extremely contaminated

3.4.4 Assessment according to Pollution load index.

Pollution load index, which is a useful tool in toxic metal pollution evaluation, refers to the number of times by which each toxic metal concentrations in the sediments (tailings) exceeded the background concentration in the soil, and it provides a summary of the overall level of toxic metal toxicity in a sample. The world average concentrations of metals using shale was used as background for identified toxic metals in this study (Turekian & Wedepohl, 1961; Santos-Francés *et al*., 2017). The PLI can provide an estimate of the various metal contamination status and precautionary steps to be taking (Angula, 1996). Using equation (4) as developed by (Turekian & Wedepohl, 1961), the PLI of the study site was calculated by obtaining the n-root from the n-CFs that was obtained for all the metals.

$$PLI = (CF1 \times CF2 \times CF3 \times \ldots \times CFn)^{1/n} \quad (4)$$

Where,

CF is the contamination factor.

CFn is the CF value of metal n.

n is the number of metals.

Interpretation of PLI values are categorized into two levels; polluted (PLI > 1) and unpolluted (PLI < 1) whereas PLI = 1 indicate trace metal loads close to the background level (Cabrera *et al*., 1999).

3.4.5 United States Environmental Protection Agency.

The potential contamination of the tailing's sediments was evaluated using the proposed sediment quality guidelines by USEPA (USEPA, 2004). **Table 3.5**. Illustrated the various criteria.

Table 3. 5 USEPA Guidelines for sediments (mg/kg dry weights) in comparison with gold mine tailings sediments.

Metal	Not polluted	Moderately polluted	Heavily polluted	Present study
Cd	…..	…..	> 6	7.1
Cr	< 25	25 – 75	> 75	860.3
Cu	< 25	25 - 50	> 50	0.1
Pb	< 40	40 - 60	> 60	121.9
Zn	< 90	90 - 200	> 200	3.9

3.5 Results and discussion.

3.5.1 Soil physical properties.

Textural properties obtained from sieve analysis of the gold mine tailings sediments using classification as prescribed by (ASTM, 2007) are presented in **Table 3.6**. These results reveal that fine sand (0.150 – 0.075 mm) and clay (0.075 - 0.053 mm) were the principal fractions of all sediment samples, with an average composition of 66.03 % for fine sand, 23.08 % clay and 10.89 % silt respectively. With the larger portion of the sediments being fine sand, there is a likelihood for nutrients accumulation is high due to the higher surface-to-volume ratios (Kaye *et al.*, 2006).

Table 3. 6 Sieve analysis of the gold mine tailings sediment samples.

Sample No.	**Sieve size (ASTM) % Materials; Retains (gms)**								
	No. 100	No. 140	No. 200	No. 270	PAN	TOTAL	% Sand	% Silt	% Clay
1	5.68	45.51	15.84	10.25	22.72	100	67.03	10.25	22.72
2	5.75	46.82	13.79	10.58	23.41	100	66.01	10.58	23.41
3	5.40	46.52	13.61	10.62	23.85	100	65.53	10.62	23.85
4	5.37	45.84	14.71	11.25	22.83	100	65.92	11.25	22.83
5	5.42	45.93	13.93	11.81	22.91	100	65.28	11.81	22.91
6	5.39	47.88	13.01	11.20	22.52	100	66.28	11.20	22.52
7	5.42	48.23	11.87	10.78	23.70	100	65.52	10.78	23.70
8	5.88	46.38	13.42	10.44	23.88	100	65.68	10.44	23.88
9	5.94	46.82	13.00	10.32	23.92	100	65.76	10.32	23.92
10	5.66	44.46	16.15	10.58	23.15	100	66.27	10.58	23.15
11	5.86	47.20	14.22	9.88	22.84	100	67.28	9.88	22.84
12	5.42	45.30	15.83	11.32	22.13	100	66.55	11.32	22.13
13	5.38	45.92	13.68	11.84	23.18	100	64.98	11.84	23.18
14	5.62	46.34	13.74	10.68	23.62	100	65.70	10.68	23.62
15	5.48	46.82	13.81	10.31	23.58	100	66.11	10.31	23.58
16	5.23	46.92	14.81	10.22	22.82	100	66.96	10.22	22.82
17	5.98	48.22	11.62	11.69	22.49	100	65.82	11.69	22.49
18	5.36	48.80	11.78	11.38	22.68	100	65.94	11.38	22.68
19	5.92	48.24	11.34	11.75	22.75	100	65.50	11.75	22.75
20	5.68	47.36	13.37	10.94	22.65	100	66.41	10.94	22.65

Geochemical properties of the sediments such as the pH, EC and carbonate content (see **Table 3.7**.) helps in ascertaining vital information to comprehend the soils potential to withhold toxic metals (Maas *et al*., 2010). The results obtained for the sediment pH measurements, showed that the study area is very strongly acidic ranging from 3.86 to 4.34. The low pH values in the study area were related with heterogeneous deposits of sulphidic residues from the mine surroundings, which resulted in low pH values that is attributed to microbial sulphide oxidation and the resultant formation of sulfuric acid (Bernhard, 2014). Nutrient uptake by plants may be inhibited by the level of acidity as most plant nutrients are optimally available to plants within 6.5 to 7.5 pH range which also support plant root growth (Matsumoto *et al*., 2017). The low CEC values which correlates with the high proportion of sand fragment is an indication that the sediments may likely not have reliable soil sorption capacity (Lambooy, 1984). LOI of studied soils were in the range of (5.0 – 5.4 %)-dry weight, which could be, attributed to growing plants within the tailing's sediments.

Table 3. 7 Geochemical properties of gold mine tailings sediments

Station No.	pH	C.E (mS/cm)	CEC (meq/100g)	LOI (%)
1	3.86	1.30	8.5	5.1
2	4.34	1.50	8.8	5.4
3	4.28	1.80	9.0	5.0
4	4.30	1.90	8.3	5.1
5	3.92	1.40	9.1	5.3
6	4.34	1.60	8.8	5.1
7	3.89	1.40	8.5	5.4
8	3.87	1.40	9.1	5.1
9	3.86	1.40	9.0	5.2
10	4.27	1.80	8.8	5.2
11	4.28	1.80	9.4	5.4
12	4.28	1.80	8.5	5.1
13	3.88	1.40	9.3	5.2
14	3.86	1.40	8.7	5.2
15	4.30	1.60	8.3	5.4
16	3.87	1.40	9.1	5.1
17	3.86	1.40	9.0	5.1
18	4.31	1.50	8.5	5.2
19	4.27	1.90	8.8	5.1
20	4.28	1.80	9.3	5.2

3.5.2 Metal content.

The summary of the determined toxic metal concentrations within the sediments of the study area by using ICP-OES are presented in **Table 3.8**. The concentration of various toxic metal varies from 860.3 – 862.6 mg/kg for Cr; 324.9 – 328.4 mg/kg for Al; 200.9 – 203.4 mg/kg for As; 130.1 – 136.2 mg/kg for Fe; 121.9 – 125.8 mg/kg for Pb; 27.3 – 30.2 mg/kg for Co; 23.8 – 26.8 mg/kg for Ni; 7.2 – 9.2 mg/kg for Ti; 7.1 – 9.2 mg/kg for Cd; 4.0 – 5.6 mg/kg for Zn and 0.1 – 0.6 mg/kg for Cu. Chromium (Cr) was identified as the most abundant toxic metal in the sediment samples. Mean concentration of the metals were Cr: 861.5 mg/kg; Al: 326.8 mg/kg; As: 202.2 mg/kg; Fe: 134.3 mg/kg; Pb: 123.7 mg/kg; Co: 28.8 mg/kg; Ni: 25.4 mg/kg; Ti: 8.5 mg/kg; Cd: 8.3 mg/kg; Zn: 4.5 mg/kg and Cu: 0.2 mg/kg dry weights. The average order of metal concentration is Cr > Al > As > Fe > Pb > Co > Ni > Ti > Cd > Zn > Cu. The mineral composition of the sediments and mining activities that took place within this region may be attributed to the high element concentrations in the soil samples.

In comparism to the interim sediment quality guidelines (ISQG) proposed by the Canadian Council of Ministers of the Environment (CCME, 2001), the elemental pollution status of the tailings (soil) were assessed **Table 3.8**. The toxic metals from the studied tailings sediments except for Zn and Cu all exceeded the ISQG. This implies that the sediments are toxic and could result in the introduction of sediment contaminants into the aquatic food web through predation by organisms at higher trophic levels.

In trace amounts, Arsenic is one of the priority toxic metals due to its several deteriorating effects to both plants and animals. The level of identified arsenic in the sediment is worrisome. As a non-essential element, Arsenic is not required for the growth of living organisms, though recent discovery reports a bacterium that replaces phosphorus with Arsenic for several cellular functions (Wolfe-Simon *et al*., 2010). Plants often accumulate Arsenic by root uptake from soil or by absorption of airborne Arsenic deposited on their leaves (USEPA, 1982). Arsenate, a dominant specie of Arsenic in soils, based on its similarity to phosphate usually compete for the same uptake carriers in the root plasmalemma of most plants. In so doing interrupts with several metabolic processes that end up inhibiting plant growth and development through arsenic-induced phytotoxicity (Marin *et al*., 1992; Marin *et al*., 1993). Some of the toxicity symptoms may include inhibition of seed germination, decrease in plant height, depressed tillering, reduction in root growth and some necrosis, decrease in shoot growth, lower fruit and grain yield, reductions in chlorophyll and protein contents, and in photosynthetic capacity and even death (Marin *et al*., 1992; Marin *et al*., 1993; Carbonell-Barrachina *et al*., 1995; Kang *et al*., 1996; Abedin *et al*., 2002).

Due to migration and expansion of residential areas into former mining territories, the danger of human exposure to soil Arsenic has risen in the last two decades which have affected adversely the health of many (Mandal *et al*., 1998). Continued exposure to Arsenic results in several clinical manifestations such as melanosis (hyperpigmentation), keratosis, and leukomelanosis (hypopigmentation) of which cutaneous lesions are the highest reported (WHO, 1998; Das & Sengupta, 2008). Arsenic is also a well-known carcinogen, causing skin, lung, bladder, liver, and kidney cancers (Program, 2011; IARC, 2012).

The average concentration of Copper (Cu) being 0.2 mg/kg was within the maximum acceptable concentration of 6.6 mg/kg for agricultural soil and safe limit of the Republic of South Africa (Herselman, 2007). As an important micronutrient, Cu is required for the growth of both plants and animals. In humans, it aids in the production of blood haemoglobin while plants utilize it in seed production, disease resistance, and regulation of water. In high levels, Cu could cause anaemia, liver and kidney damage, as well as stomach and intestinal irritation (Wuana & Okieimen, 2011). Cu typically occurs in drinking water from Cu pipes, as well as from additives intended to control algal growth. The interaction of Cu with the environment is complex, however different studies revealed that most Cu introduced into the environment rapidly becomes, stable and results in a form which does not pose a danger to the environment (Eriksson *et al*., 1997; Martinez & Motto, 2000).

Zinc is an important metal due to its enzymatic and regulatory functions in biological systems. Being a readily mobile element, Zinc (Zn) when in high doses exhibit toxic and carcinogenic effects that could result in serious haematological and neurologic complications, liver and kidney disorders, hypertension, gastrointestinal misery, loose bowels, pancreatic harm and ailments in both humans and animals (Roa *et al*., 2001). On the earth crust, Zinc is found in an average concentration of 80 mg/kg in association with ores of other metals such as Pb, Cu and Cd (Ghazban *et al*., 2014).

Chromium (Cr) has an average concentration of 100 mg/kg in the earth crust and the only known ore of commercial value is chromite ($FeO.Cr_2O_4$). Contamination by Cr could result in toxicity in plants depending on its state of valency since Cr (VI) due to its being highly mobile is toxic, while Cr (III) as less mobile is less toxic. The subsequent uptake, translocation, and accumulation of Cr by plants is dependent on its speciation. Cr in its trivalent (III) and hexavalent (VI) forms are known to be of biological importance. Generally, Cr poses the greatest threat to humans, animals and plants. Decreased seed germination, reduction of growth, decreased yield, inhibition of enzymatic activities, impairment of photosynthesis, nutrient and oxidative imbalances, and mutagenesis are some of the symptoms of Cr toxicity in plants (Helena, 2012). In previous studies, the toxicity of Cr (VI), Cr (III), and Cr tannery sludge were compared with respect to Cr mobility in soil and toxicity in wheat, oat, and sorghum plants and findings were that Cr(VI) was more mobile in soil and caused higher toxicity on those plant seedlings, while tannery sludge was the least toxic (López-Luna *et al*., 2009; Kanu & Sudipta, 2018). In humans, prolonged exposure results in kidney and liver disorders (Scragg, 2006).

Lead (Pb) is the largely known immobile nonessential element among the toxic metals with most of its compounds being noxious in nature. Pb on the earth crust has an average concentration of 0.1 mg/kg. There is a gradual phase out of Pb from the materials regularly used by humans due to it being a metal toxicant. Mostly via food chain, Pb penetrates human or animal metabolism. The observed Pb content within the samples was very high and have been reported globally to be very harmful to humans and other animals as a long-term exposure could result in the bioaccumulation and biomagnification that end up in serious neurological health challenges. In plants, concentrations above 5 mg/kg of Pb causes severe growth retardation, discolouration, and morphological deformities. Pb accumulates in the body organs (i.e., brain), which may lead to poisoning or even death. The presence of lead often affects the gastrointestinal tracts, kidneys, and central nervous system. Infants exposed to lead are likely to suffer impaired development, lower IQ, shortened attention span, hyperactivity, and mental deterioration (Baldwin & Marshall, 1999). Adults usually suffer decreased reaction time, loss of memory, nausea, insomnia, anorexia, and weakness of the joints when exposed to Pb (NSC, 2009). Lead performs no known essential function in the human body, it can merely do harm after uptake from food, air, or water.

Industrial waste materials, lime, fertilizer and sewage sludge constitute the major sources of nickel into soils (Mcllveen & Negusanti, 1994). Till date, nickel (Ni) remains a toxic metal of environmental concern as a result of decreased soil pH, due to reduced use of soil liming in agricultural soils and mobilization arising from increased acid rain in industrialized areas (Cempel & Nikel, 2006). With decreasing pH, Ni exhibits increased solubility and mobility, thus, soil pH is the major factor controlling its solubility, mobility and sorption, while clay content, iron-manganese mineral and soil organic matter are of secondary importance (Tye *et al*., 2004). Nickel (Ni) concentrations were observed to be high which could result in toxic effects to both plants and animals due to its ability to replace other metal ions in enzymes, proteins or bind to cellular compounds (Cempel & Nikel, 2006). Nickel (Ni) is reported to interact with at least 13 essential elements namely calcium, chromium, cobalt, copper, iodine, iron, magnesium, manganese, molybdenum, phosphorus, potassium, sodium and zinc (Nielsen, 1980). As a result, prolong exposure of humans to oxides and sulphides of nickel is linked with possible risk to lung and nasal tumors, skin allergies, nasal sinusitis, rhinitis and dermatitis (Rahman *et al*., 2012). Symptoms of nickel toxicity in plants besides inhibited growth include chlorosis, stunted root growth and brown interveinal necrosis (Uren, 1992).

Cadmium (Cd) is being discussed on a global platform as one of the most eco-toxic metals with a tendency of adversely affecting biological activities, plant metabolism, soil health and human health. The usage of Cadmium (Cd) is widely seen in Ni/Cd batteries, as rechargeable or secondary power sources exhibiting high output, long life, low maintenance, and high tolerance to physical and electrical stress. Observed levels of Cadmium was high and of great concern because it is very biopersistent and, once absorbed by an organism, remains resident for many years. In humans, Cadmium is known to affect several enzymes. Previous research revealed that renal damage that results in proteinuria is the consequence of Cd adversely affecting enzymes responsible for reabsorption of proteins in kidney tubules (Fasinu & Orisakwe, 2013). A prolong exposure to this metal even at very low concentration also reduces the activity of delta-aminolaevulinic acid synthetase, arylsulfatase, alcohol dehydrogenase, and lipoamide dehydrogenase, which often cause anaemia, cardiovascular disorders and hypertension whereas it enhances the activity of delta-aminolaevulinic acid dehydratase, pyruvate dehydrogenase, and pyruvate decarboxylase (Manahan, 2003).

Table 3. 8 Mean of toxic metals concentration (mg/kg dry weight) in gold mine tailings sediments.

Station No.	Cr	Al	As	Fe	Pb	Co	Ni	Ti	Cd	Zn	Cu
1	862.6	327.4	201.7	134.1	125.6	28.4	26.1	9.0	9.2	4.7	0.6
2	860.4	327.9	203.4	136.2	122.9	30.2	25.3	8.3	8.8	4.0	0.1
3	861.3	328.0	202.9	133.7	123.1	29.5	26.4	9.2	8.1	4.1	0.2
4	862.4	328.4	202.4	130.1	124.7	28.8	24.7	8.1	7.9	3.9	0.2
5	862.1	326.5	202.1	132.5	121.9	29.6	23.8	8.7	7.2	5.6	0.3
6	861.5	325.7	201.7	134.9	122.1	29.3	25.1	7.9	8.3	4.3	0.1
7	860.6	324.9	203.0	135.3	123.5	28.7	25.7	8.5	7.5	5.2	0.1
8	861.1	328.1	201.9	135.1	123.2	29.2	26.3	9.0	7.9	4.9	0.3
9	860.7	327.9	202.6	135.9	124.1	27.5	26.8	9.2	9.0	4.2	0.1
10	860.3	326.3	202.1	132.7	124.8	29.1	25.2	8.1	8.5	5.1	0.1
11	860.6	325.4	201.7	136.0	122.3	27.3	25.7	8.3	7.1	5.3	0.1
12	861.0	326.7	200.9	131.8	122.5	27.9	23.9	8.7	8.7	5.0	0.2
13	862.1	326.1	201.2	135.9	124.9	28.7	24.3	7.6	8.3	5.5	0.6
14	860.5	327.9	201.4	134.1	123.1	28.3	26.0	9.1	9.1	4.5	0.1
15	862.5	328.2	203.0	133.7	122.7	28.0	25.8	9.2	8.3	5.0	0.2
16	862.3	326.3	202.6	134.9	125.8	29.1	24.6	8.3	8.5	5.3	0.3
17	862.4	325.9	201.5	133.5	123.7	29.5	24.2	8.0	8.1	4.1	0.1
18	861.9	327.4	202.3	134.2	125.1	29.7	26.5	7.2	8.0	4.8	0.4
19	861.6	326.1	201.9	134.9	124.3	28.1	25.7	8.4	8.5	4.4	0.5
20	862.0	325.6	203.1	135.7	125.3	28.4	26.3	8.7	8.8	4.6	0.1
Mean	861.5	326.8	202.2	134.3	123.7	28.8	25.4	8.5	8.3	4.5	0.2
Max	862.6	328.4	203.4	136.2	125.8	30.2	26.8	9.2	9.2	5.6	0.6
Min	860.3	324.9	200.9	130.1	121.9	27.3	23.8	7.2	7.1	3.9	0.1
B_n	90	88000	13	47200	20	19	50	4600	0.3	95	45
ISQG	52.3	NA	7.24	NA	30.2	NA	NA	NA	0.7	124.0	18.7

3.5.3 Pollution status.

The assessment of the overall contamination of the studied area was based on the contamination factor **Table 3.9**. The average contamination factor for single metal from this study revealed the sediments as slightly contaminated with Ni and Zn, moderately contaminated with Co and highly contaminated with Cr, As, Pb and Cd. The highest average contamination factor value was that of Cd (27.63). Overall, the degree of contamination values of the sediments from the study site indicate very high contamination.

The average index of geo-accumulation values and contamination levels from the various sampling points within the study area as shown on **Table 3.10** reveals an uncontaminated status for Co (0.01), Ni (-1.09) and Zn (-3.39) respectively. However, Cr and Pb within the area showed a moderately contamination level with average I_{geo} values being 1.85 and 1.42 respectively. The site was however moderately to strongly contaminated with As (2.34) and Cd (2.91).

As indicated in **Table 3.10**, Pollution load index (PLI) ranged from 2.56 – 2.75, with mean value 2.67. PLI values of the different stations are above 1 which strongly indicate that the sediments are all polluted by toxic metals, an indication of deterioration of the study site.

It is evident from the present study that the abandoned gold mine tailings site is not polluted with Zn and Cu, but heavily polluted with Cd, Cr and Pb when evaluated by comparison with the sediment quality guideline proposed by USEPA.

Table 3. 9 Contamination factor (CF) and Degree of contamination at various sampling station at the Blesbokspruit abandoned gold mine tailings site.

	Contamination factor of single metal								
Station No.	**Cr**	**As**	**Pb**	**Co**	**Ni**	**Cd**	**Zn**	**Degree of contamination**	
1	9.58	15.52	6.28	1.49	0.52	30.67	0.05	64.11	Very high
2	9.56	15.65	6.15	1.59	0.51	29.33	0.04	62.83	Very high
3	9.57	15.61	6.16	1.55	0.53	27.00	0.04	60.46	Very high
4	9.58	15.57	6.24	1.52	0.49	26.33	0.04	59.77	Very high
5	9.58	15.55	6.10	1.56	0.48	24.00	0.06	57.33	Very high
6	9.57	15.52	6.11	1.54	0.50	27.67	0.05	60.96	Very high
7	9.56	15.62	6.18	1.51	0.51	25.00	0.05	58.43	Very high
8	9.57	15.53	6.16	1.54	0.53	26.33	0.05	59.71	Very high
9	9.56	15.58	6.21	1.45	0.54	30.00	0.04	63.38	Very high
10	9.56	15.55	6.24	1.53	0.50	28.33	0.05	61.76	Very high
11	9.56	15.52	6.12	1.44	0.51	23.67	0.06	56.88	Very high
12	9.57	15.45	6.13	1.47	0.48	29.00	0.05	62.15	Very high
13	9.58	15.48	6.25	1.51	0.49	27.67	0.06	61.04	Very high
14	9.56	15.49	6.16	1.49	0.52	30.33	0.05	63.60	Very high
15	9.58	15.62	6.14	1.47	0.52	27.67	0.05	61.05	Very high
16	9.58	15.58	6.29	1.53	0.49	28.33	0.06	61.86	Very high
17	9.58	15.50	6.19	1.55	0.48	27.00	0.04	60.34	Very high
18	9.58	15.56	6.26	1.56	0.53	26.67	0.05	60.21	Very high
19	9.57	15.53	6.22	1.48	0.51	28.33	0.05	61.69	Very high
20	9.58	15.62	6.27	1.49	0.53	29.33	0.05	62.82	Very high
Average	9.57	15.55	6.19	1.51	0.51	27.63	0.05	61.01	Very high

Table 3. 10 Geo-accumulation index (Igeo) and Pollution load index (PLI) at various sampling station at the Blesbokspruit abandoned gold mine tailings site.

Station No.	Cr	As	Pb	Co	Ni	Cd	Zn	PLI	Description of PLI
1	1.85	2.34	1.43	0.00	-1.05	3.02	-3.51	2.72	Polluted
2	1.85	2.34	1.41	0.06	-1.09	2.97	-3.51	2.63	Polluted
3	1.85	2.34	1.41	0.04	-1.05	2.89	-3.51	2.61	Polluted
4	1.85	2.34	1.43	0.01	-1.11	2.87	-3.51	2.56	Polluted
5	1.85	2.34	1.40	0.04	-1.14	2.77	-3.22	2.67	Polluted
6	1.85	2.34	1.40	0.03	-1.11	2.91	-3.51	2.67	Polluted
7	1.85	2.34	1.42	0.01	-1.08	2.81	-3.22	2.64	Polluted
8	1.85	2.34	1.41	0.02	-1.05	2.87	-3.51	2.68	Polluted
9	1.85	2.34	1.42	-0.04	-1.02	3.00	-3.51	2.63	Polluted
10	1.85	2.34	1.43	0.02	-1.08	2.94	-3.22	2.68	Polluted
11	1.85	2.34	1.41	-0.04	-1.08	2.76	-3.22	2.66	Polluted
12	1.85	2.33	1.41	-0.02	-1.14	2.96	-3.22	2.65	Polluted
13	1.85	2.34	1.43	0.01	-1.14	2.91	-3.22	2.73	Polluted
14	1.85	2.34	1.41	-0.01	-1.05	3.01	-3.51	2.71	Polluted
15	1.85	2.34	1.41	-0.02	-1.08	2.91	-3.22	2.67	Polluted
16	1.85	2.34	1.43	0.02	-1.11	2.94	-3.22	2.75	Polluted
17	1.85	2.34	1.42	0.04	-1.14	2.89	-3.51	2.57	Polluted
18	1.85	2.34	1.43	0.04	-1.05	2.88	-3.51	2.69	Polluted
19	1.85	2.34	1.42	-0.01	-1.08	2.94	-3.51	2.68	Polluted
20	1.85	2.34	1.43	0.00	-1.05	2.97	-3.51	2.71	Polluted

3.6 Conclusion.

The successful assessment of trace metal contamination of the abandoned gold mine tailings at Blesbokspruit-Ekurhuleni was done using indices such as geo-accumulation index, contamination factor, and degree of contamination and pollution load index. The sediment was mostly dominated by fine sand and silt/clay. Based on sediment quality guidelines proposed by the USEPA, the contamination of the sediment by Zn and Cu was negligible while Cd, Cr and Pb were detected at high concentrations. The evaluated pollution load index indicated that the sediments in the tailings dump are polluted while the geo-accumulation index revealed that Cr, Pb, and As contaminated the site, thus indicating very high degrees of contamination of the sediments at the mine dump. The high metal contaminants could be attributed to anthropogenic activities from previous extensive gold mining activities that took place within the area. Considering agricultural activities and human dwellers within the surrounding areas of the mine tailings, there are high tendencies of deleterious impacts. As a further precaution, this study strongly supports the call for analysis of the stream and drinking water quality, including the staple crops that are cultivated within the vicinity of the dump site, to ascertain the levels of toxic metals within such crops. Stringent mitigation plans or conversion of the tailings into value-added products should be considered.

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References.

Abedin, M.J., Cottep-Howells, J., & Meharg, A.A. 2002. Arsenic uptake and accumulation in rice (Oryza sativa L.) irrigated with contaminated water. Plant Soil, 240, 311–319.

Ahdy, H.H.H., & Khaled, A. 2009. Heavy Metals Contamination in Sediments of the Western Part of Egyptian Mediterranean Sea. Australian Journal of Basic and Applied Sciences, 3 (4), 3330-3336, ISSN 1991-8178.

Akoto, O., Ephraim, J.H., & Darko, G. 2008. Heavy Metal Pollution in Surface Soils in the Vicinity of Abundant Railway Servicing Workshop in Kumasi, Ghana. International Journal of Environmental Resources, 2, 359-364.

AngloGold Ashanti. 2004. Case studies; Woodlands Project – good progress being made with phytoremediation project. Environment – AngloGold Ashanti Report to Society.

Angula, E. 1996. The Tomlinson Pollution Index applied to heavy metal, Mussel-Watch data: A useful index to assess coastal pollution. Science of the Total Environment, 187, 19-56.

Aris, A.Z., Ismail, F.A., Ng, H.Y., & Praveena, S.M. 2014. An Experimental and Modelling Study of Selected Heavy Metals Removal from Aqueous Solution Using *Scyllaserrataas* Biosorbent. Pertanika Journal of Science & Technology 22 (2), 553 – 566.

ASTM D422-63. 2007. Standard Test Method for Particle-Size Analysis of Soils.

Baldwin, D.R., & Marshall, W.J. 1999. Heavy metal poisoning and its laboratory investigation. Annals of Clinical Biochemistry, 36 (3), 267–300.

Barbieri, M. 2016. The Importance of Enrichment Factor (EF) and Geoaccumulation Index (Igeo) to Evaluate the Soil Contamination. Journal of Geology Geophysics 5: 237.

Barkouch, Y., & Pineau, A. 2016. Evaluation of the impact of mine activity on surrounding soils of Draa Lasfar mine in Marrakech- Morocco. African Journal of Environmental Science and Technology. 10 (1), 44-49.

Bernhard, D. 2014. Evolution of Acid Mine Drainage Formation in Sulphidic Mine Tailings. Minerals, 4, 621-641; doi:10.3390/min4030621.

BIO Intelligence Service. 2014. Soil and water in a changing environment, Final Report prepared for European Commission (DG ENV), with support from HydroLogic.

Cabrera, F., Clemente, L., & Barrientos, D.E. 1999. Heavy metal pollution of soils affected by the guadiamar toxic flood. The Science of the Total Environment. 242 (1-3), 117 – 129.

Canadian Council of Ministers of the Environment (CCME). 2001. Canadian sediment quality guidelines for the protection of aquatic life, Polychlonnated dioxins and furans (PCDD/Fs) In Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Carbonell-Barrachina, A.A., Burlo-Carbonell, F., & Mataix-Beneyto, J. 1995. Arsenic uptake, distribution and accumulation in tomato plants: effect of arsenic on plant growth and yield. Journal of Plant Nutrition, 18, 1237–1250.

Cempel, M., & Nikel, G. 2006. Nickel: A review of its sources and Environmental Toxicology. Polish Journal of Environmental Studies, 15 (3), 375-382.

Das, N.K., & Sengupta, S.R. 2008. Arsenicosis: diagnosis and treatment. Indian Journal of Dermatology, Venereology and Leprology, 74(6):571–81.

Ebenebe, P.C., Shale, K., Sedibe, M., Tikilili, P., & Achilo, M.C. 2017. South African Mine Effluents: Heavy Metal Pollution and Impact on the Ecosystem. International Journal of Chemical Sciences; 15 (4), 198.

Ekurhuleni Metropolitan Municipality (EMM). 2007. Environmental management framework for Ekurhuleni. Ekurhuleni.

Eriksson, J., Andersson, A., & Andersson, R. 1997. The state of Swedish farmlands. Swedish Environmental Protection Agency, Stockholm, Sweden, Technical Report 4778.

Fasinu, P.S., & Orisakwe, O.E. 2013. Heavy Metal Pollution in Sub-Saharan Africa and Possible Implications in Cancer Epidemiology (A Review). Asian Pacific Journal of Cancer Prevention,14 (6), 3393-3402.

Figueroa, F., Castro-Larragoitia, J., Aragón, A., & García-Meza, J. 2010. Grass cover density and metal speciation in profiles of a tailings-pile from a mining zones in Zacatecas, North-Central Mexico. Environmental Earth Sciences, 60 (2), 395-407.

Ghazban, F., Parizanganeh, A., Zamani, A., & Taghilou, B. 2014. Assessment of Heavy Metal Pollution in Water and Sediments from the Ghalechay River, Baychebagh Copper Mine Area, Iran. Soil and sediment contamination, 24 (2), 172 – 190.

Hakanson, L. 1980. An ecological risk index for aquatic pollution control. A sedimentological approach. Water Research. 14 (8), 975-1001.

Helena, O. 2012. Chromium as an Environmental Pollutant: Insights on Induced Plant Toxicity. Journal of Botany, Article ID 375843; https://doi.org/10.1155/2012/375843.

Herselman, J.E. 2007. The concentration of selected trace metals in South African soils. Dissertation presented for the degree of Doctor of philosophy, Department of Soil Science, University of Stellenbosch, South Africa.

International Agency for Research on Cancer (IARC). 2012. A review of human carcinogens: arsenic, metals, fibres, and dusts. Lyon: World Health Organization Press.

Jahan, I., Hoque, S., Ullah, S.M., & Kibria, M.G. 2003. Effects of arsenic on some growth parameters of rice plant. Dhaka University Journal of Biological Sciences, 12, 71–77.

Kang, L.J., Li, X.D., Liu, J.H., & Zhang, X.Y. 1996. The effect of arsenic on the growth of rice and residues in a loam paddy soil. Journal of the Jilin Agricultural University, 18, 58–61.

Kanu, S., & Sudipta, P. 2018. Metabolic adaptability in hexavalent chromium-treated renal tissue: an in vivo study. Clinical Kidney Journal, 11 (2), 222–229.

Kaye, J.P., Groffman, P.M., Grimm, N.B., Baker, L.A., & Pouyat, R.V. 2006. A distinct urban biogeochemistry. Trends in Ecology & Evolution, 21, 192-199.

Lambooy, A.M. 1984. Relationship between cation exchange capacity, clay content and water retention of Highveld soils, South African Journal of Plant and Soil, 1 (2), 33-38.

Landers, J.E. 2016. Aquatic food webs and heavy metal contamination in the upper Blackfoot River, Montana. Graduate Student Theses, Dissertations, & Professional Papers. 10719.

Loureiro, S., Ferreira, A., Soares, A., & Nogueira, A. 2005. Evaluation of the toxicity of two soils from Jales Mine (Portugal) using aquatic bioassays. Chemosphere 61, 168-177.

López-Luna, J., González-Chávez, M.C., Esparza-García, F.J., & Rodríguez-Vázquez, R. 2009. Toxicity assessment of soil amended with tannery sludge, trivalent chromium and hexavalent chromium, using wheat, oat and sorghum plants. Journal of Hazardous Materials, 163 (2-3), 829–834.

Maas, S., Scheifler, R., Benslama, M., Crini, N., Lucot, E., Brahmia, Z., Benyacoub, S., & Giraudoux, P. 2010. Spatial distribution of heavy metal concentrations in urban, suburban and agricultural soils in a Mediterranean city of Algeria. Environmental Pollution, 158, 2294–2301.

Manahan, S.E. 2003. Toxicological Chemistry and Biochemistry, CRC Press, Limited Liability

Company (LLC), Boca Raton, Florida 33431, 3rd edition.

Mandal, B.K., Chowdhury, T.R., Samanta, G., Mukherjee, D., Chanda, C.R., & Saha, K.C. 1998. Impact of safe water for drinking on five families for 2 years in West Bengal, India. Science of the Total Environment, 218, 185–201.

Mann, R.M., Vijver, M.G., & Peijnenburg, W.J.G.M. 2011. Metals and Metalloids in Terrestrial Systems: Bioaccumulation, Biomagnification and Subsequent Adverse Effects. Ecological Impacts of Toxic Chemicals, 43-62.

Marin, A.R., Pezeshki, S.R., Masscheleyn, P.H., & Choi, H.S. 1993. Effect of dimethylarsinic acid (DMAA) on growth, tissue arsenic and photosynthesis of rice plants. Journal of Plant Nutrition, 16, 865–80.

Marin, A.R., Masscheleyn, P.H., & Patrick Jr, W.H. 1992. The influence of chemical form and concentration of arsenic on rice growth and tissue arsenic concentration. Plant Soil,139, 175–83.

Martínez, C.E., & Motto, H.L. 2000. Solubility of lead, zinc and copper added to mineral soils. Environmental Pollution, 107 (1), 153–158.

Matsumoto, S., Shimada, H., Sasaoka, T., Miyajima, I., Kusuma, G.J., & Gautama, R.S. 2017. Effects of Acid Soils on Plant Growth and Successful Revegetation in the Case of Mine; Soil pH for Nutrient Availability and Crop Performance, IntechOpen, 9 -27; doi: 10.5772/intechopen.70928

McLaughlin, M.J., Zarcinas, B.A., Stevens, D.P., & Cook, N. 2000. Soil testing for heavy metals. Communications in Soil Science and Plant Analysis, 31 (11–14), 1661–1700.

Mcllveen, W.D., & Negusanti, J.J. 1994. Nickel in terrestrial environment. Science of the Total Environment, 148, 109-138.

Muhammad, S., Tahir Shah, M., & Khan, S. 2011. Heavy metal concentrations in soil and wild plants growing around Pb-Zn sulfide terrain in the Kohistan region, northern Pakistan. Microchem. Journal. 99, 67-75.

Muller, G. 1969. Index of geo-accumulation in sediments of the Rhine River. GeoJournal, 2, 108-118.

National Safety Council (NSC). 2009. Lead Poisoning.

Nielsen, F.H. 1980. Interaction of Nickel with essential minerals. In Nickel in the Environment, J.O Nriagu (Ed), John Wiley & Sons, New York, 611- 634.

Nilin, J., Moreira, L. B., Aguiar, J. E., Marins, R., Moledode Souza Abessa, D., Cruz Lotufo, T. M. D., et al. 2013. Sediment quality assessment in a tropical estuary: The case of Ceará River, Northeastern Brazil. Marine Environmental Research, 91, 89–96.

Oelofse, S.H.H., Hobbs, P.J., & Rascher, J. 2007. The pollution and destruction threat of gold mining waste on the Witwatersrand –A West Rand case study. Symposium on Environmental Issues and Waste Management in Energy and Mineral Production, Bangkok.

Okereafor, G.U., Mulaba-Bafubiandi, A.F., Sebola, T.E., Uche-Okereafor, N.C., & Mavumengwana, V. 2018. The effects of an acidic environment on selected geophagic clayey samples and its impact on the bioavailability of certain elements. Transaction of the Royal Society of South Africa. 73 (2), 180 – 185.

Program, N.T. 2011. Report on carcinogens. 12th ed. Research Triangle Park: NTP.

Rahman, S.H., Khanam, D., Adyel, T.M., Islam, M.S., Ahsan, M.A., & Akbor, M.A. 2012. Assessment of heavy metal contamination of agricultural soil around Dhaka Export Processing Zone (DEPZ), Bangladesh: Implication of seasonal variation and indices.

Applied Science. 2, 584 – 601.

Roa, M.S., Gopalkrishnan, R., & Venkatesh, B.R. 2001. Medical geology – An emerging field in environmental science. In National Symposium on Role of Earth Sciences, Integrated and Related Societal Issues, Lucknow, India, 2 – 4 November, GSI Special Publication. No. 65, 213 – 222.

Robertson, S. 2011. Direct Estimation of Organic Matter by Loss on Ignition: Methods. SFU Soil Science Lab.

Santos-Francés, F., Martínez-Graña, A., Rojo, P.A., Sánchez, A.G. 2017. Geochemical Background and Baseline Values Determination and Spatial Distribution of Heavy Metal Pollution in Soils of the Andes Mountain Range (Cajamarca-Huancavelica, Peru). International Journal of Environmental Research and Public Health, 14, 859.

Schwegler, F. 2006. Air quality management: A mining perspective. In: Air Pollution XIV, Longhurst JWS, Brebbia C A, editors. WIT Transactions on Ecology and the Environment. WIT Press, Southampton, UK.

Shafie, N.A., Aris, A.Z., Zakaria, M.F., Haris, H., Yinglini, W., & Isa, N.M. 2013. Application of Geoaccumulation index and enrichment factors on the assessment of heavy metal pollution in sediments. Journal of Environmental Science and Health Part A: Toxic Hazardous Substances and Environmental Engineering 48 (2), 182-190.

Sharma, R.K., Agrawal, M., & Marshall, F. 2007. Heavy metal contamination of soil and vegetables in suburban areas of Varanasi, India. Ecotoxicology and Environmental Safety. 66 (2), 258-266.

Song, Y., Ji, J., Mao, C., Yang, Z., Yuan, X., Ayoko, G.A., & Fros, R.L. 2010. Heavy metal contamination in suspended soils of Changjiang River – environmental implications.

Geoderma. 159, 286-295.

Tomlinson, D.L., Wilson, J.G., Harris, C.R., & Jeffrey, D.W. 1980. Problems in the assessment of Heavy metal levels in estuaries and the formation of a pollution index. Heligolander Meeresunters. 33, 566 - 575. https://doi.org/10.1007/BF02414780

Turekian, K.K., & Wedepohl, D.H. 1961. Distribution of the Elements in Some Major Units of the Earth's Crust. Geological Society of America Bulletin. 72 (2), 175 – 192.

Tye, A.M., Young, S., Crout, N.M.J., Zhang, H., Preston, S., Zhao, F.J., & McGrath, S.P. 2004. Speciation and solubility of Cu, Ni and Pb in contaminated soils. European Journal of Soil Science, 55, 579- 590.

United States Environmental Protection Agency (USEPA). 2004. Abandoned mine lands team.

United States Environmental Protection Agency (USEPA). 1982. An exposure and risk assessment for arsenic. Washington, DC: Office of Water Regulations and Standards, EPA-440/4-85-005.

Uren, N. 1992. Forms, reactions and availability of Ni in soils. Advances in Agronomy, 48, 141-195.

Wolfe-Simon, F., Blum, J.S., Kulp, T.R., Gordon, G.W., Hoeft, S.E., & Pett-Ridge, J. 2010. A bacterium that can grow by using arsenic instead of phosphorus. Science, 332 (6034), 1163–1166.

World Health Organization (WHO). 1998. Guidelines for drinking-water quality, addendum to volume 1: recommendations. Geneva.

Wuana, R.A., & Okieimen, F.E. 2011. Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. International Scholarly Research Network (ISRN) Ecology. doi:10.5402/2011/402647.

Xiao-san, L., Shen, Y., Yong-guan, Z., & Xiang-dong, L. 2011. Trace Metal Contamination in Urban Soils of China. Science of The Total Environment 421-422, 17-30.

CHAPTER 4

RESULTS

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Mobility of trace element contaminants from abandoned gold mine dump to stream waters in an agricultural active area.

4.0 Abstract.

In this study, the selected streams within the Blesbokspruit located in South Africa were characterized. Because of prolonged mining activities coupled with ineffective management practices, several mine tailing dumps are widely distributed in this area. Metals and metalloids contamination from these tailing facilities have been reported to be major contributors to environmental hazards such as Acid Mine Drainage (AMD). With increased agricultural activities in this area, an assessment of the general quality of water being utilized for irrigation purposes and feeding of farm animals becomes inevitable. A procedural method was implemented in a bid to identify relations between tailing and stream water contamination. Representative gold tailing sediments and water samples were collected respectively. With the aid of X-ray fluorescence (XRF) and X-ray diffraction (XRD), the mineralogical characterization of the tailing sediments was successfully carried out while acid digestion using inductively coupled plasma-optical emission spectrometry (ICP-OES) was utilized in the determination of trace metal contents. Samples of different water sources were also characterized. There was a clear description of the link between tailings, water contamination and possible implications to animals and humans in a long run.

Key words: Contamination, livestock, acid mine drainage, water quality.

4.1 Introduction.

The mining of minerals such as gold, coal, titanium and other natural resources play several roles in South Africa's emerging economy with many positive outcomes as well as negative consequences. Till date, the mining sector remains the largest employer of labour. Mining of various minerals is a common sight in the country but of late has become a public menace due to land degradation and contamination of major water bodies through the discharge of waste materials such as overburdens, waste rocks, tailings, slags, mine water and gaseous wastes. The resource being mine, geology of an area and technology adopted are some of the factors that influence the nature, characteristic properties and level of mine waste generated at specific mines. Mining companies in South Africa due to legislations and regulations pertaining to general waste management at mining sites, endeavour to manage waste generated during their operations in a bid to avoid the release of contaminants into the environment (Matinde *et al*., 2018). Unfortunately, some level of contaminants, which constitute crushed, sand-like materials still find their way into the ecosystem.

By definition, mine dumps also known as residue stockpiles, refers to any debris, discard, tailing, slimes, screening, slurry, waste rock, foundry sand, beneficiation plant waste, ash or any other product derived from or incidental to a mining operation and which is stockpiled, stored or accumulated for potential re-use, or which is disposed of, by the holder of a mining right, mining permit, production right or an old order right (MPRDA, 2002; Puell, 2017). Generally, mine wastes are unwanted, currently uneconomic, solid and liquid materials found at or near mine sites that largely constitute one of the world's major waste streams due to their composition of high concentrations of elements and compounds that impact negatively on humans and animals, the surrounding environment and plants alike (Hudson-Edwards *et al*., 2011). An alarming number of mine dumps often characterized by a complex mixture of metals and dust particles are located at several jurisdiction of the country. This implies that during windy conditions, exposure to dust could be high for close-by inhabitants. Other challenging issues associated with mine wastes include environmental impacts such as the loss of agricultural lands because of their conversion to waste storage facilities, and the successive introduction of sediments and other impurities into adjoining surface and groundwater from water running over exposed chemically reactive wastes (McKinnon, 2002; Jordan, 2004; Sloss, 2017; Aznar-Sánchez et al., 2018).

Most mine wastes have trace metals (TMs) as a major component and their continued circulation in soil and water puts the world in a dangerous state due to their toxic and deleterious effects (Okereafor *et al*., 2017). TMs such as Cadmium (Cd), Thallium (Ti), Zinc (Zn), Lead (Pb), Arsenic (As), mercury (Hg), Chromium (Cr), Copper (Cu), Lead (Pb), Iron (Fe), Nickel (Ni) are naturally occurring components of the earth's crust and are often referred to as metallic chemical elements with a relatively high density - at least five times the specific gravity of water (Obodo, 2004). At low concentrations, TMs such as Cu, Cr^{3+}, Zn, Mn, Co and molybdenum (Mo) are of biological significance, however long-term exposures and high concentrations impacts negatively on several biomolecules. It is noteworthy to mention that at very low concentrations, Hg, Cd, Cr^{6+}, As and Pb stand to be very toxic (Rahman & Singh, 2016).

Sediments are vital components of aquatic habitat as they can retain contaminants that are not bioavailable to humans (Nemati *et al*., 2011). Pollutants are released into water bodies via processes such as sediments resuspension, desorption, and redox reactions of sorptive substances. This further explains why sediments despite being reservoirs could at the same time act as likely source of pollutants in the aquatic system (Nemati *et al*., 2011; Varol, 2011). Mine tailings having the possibilities of containing some TMs are seen in different areas of Blesbokspruit in Ekuhurleni Municipality, South Africa. Over the years, these mine tailings solidify leaving mountainous structures made of very fine sand particles. Several agents of erosion such as wind and surface run-off after heavy rainfall transport sediments to surrounding water bodies (rivers). These rivers are major sources of water supply to agricultural lands and may constitute diverse environmental problems to humans, animals and plants (Alomary & Belhadj, 2007).

A comprehensive understanding of the physicochemical features of soil and water pollutants provides a platform for careful soil management aimed at reducing the adverse effect of the pollutants on the ecosystem. Trace metals from mine tailings in ionic solutions sometimes contaminate groundwater via leaching and are absorbed by plants, thus introduced to the food chain (Calace *et al*., 2002). In other instance, animals drink from stream waters containing these TMs. The final consumption of these plants and animals is of great concern due to danger of TM toxicity.

South Africa's Agricultural sector had suffered immense setbacks in recent past owing to issues of water shortages and the problem of acid mine drainage (AMD) amongst others. These issues over the years have impacted adversely on the quality and quantity of farm produce. Due to irregular municipal water supply, farmers suffer economically in the quest for portable water; thus, end up relying on surrounding stream water for their farming activities. Following the growing numbers of small scale farming in the Blesbokspruit area of Ekuhurleni, this study seek to investigate the physicochemical features of selected stream waters and sediments from an abandoned gold mine tailings site with the goal of assessing the distribution of TMs in stream water and sediments from surrounding mining sites and the ecological risks of such TMs.

4.2 Sampling and samples.

4.2.1 Description of the sampling site.

Due to outraging scarcity of water resources, South Africa is referred as a semi-arid nation. Study materials were obtained from a mine tailings dump facility located within the Blesbokspruit catchment (26°10′12″S 28°27′52″E), Heidelberg (34°01′59″S 18°52′28″E) and Suikerbosrand (26°29′46″S 28°21′00″E) rivers respectively all of which constitutes part of the Vaal River Barrage secondary catchment, located in the eastern region of the Gauteng Province.

The Blesbokspruit catchment has in it an important and international wetland covering an area of about 1858 km^2 with a Rasmar recognition dated as far back as 1986. This wetland has a gold mine tailings dump located very close to it and provides support and habitat to several species of birds and plants (Pillay *et al*., 2014). Extended part of the study area is used for agricultural activities such as cultivation of crops and rearing of animals. The sampling sites (**Fig. 4.1**) were selected due to what seems to be the ironic presence of an abandoned gold mine tailing dump that has located next to it an artificial wetland. The wetland was supposed to aid in remediation of the discharge from the mines. In addition, an informal settlement characterized with mostly rural-urban dwellers that engage in farming activities was also in proximity. The rivers being considered in this study are to the best of our knowledge the major water sources for farming activities such as irrigation and feeding of local cows. The subsistence farmers within this area created artificial channels in a bid to redirect water from the streams to special reservoirs that service mostly the animals (**Fig. 4.2**). During rainfall and often windstorms, sediments from the tailing dumps get eroded into the wetland and subsequently into the surrounding rivers because of wind mode of transportation (**Fig. 4.3**).

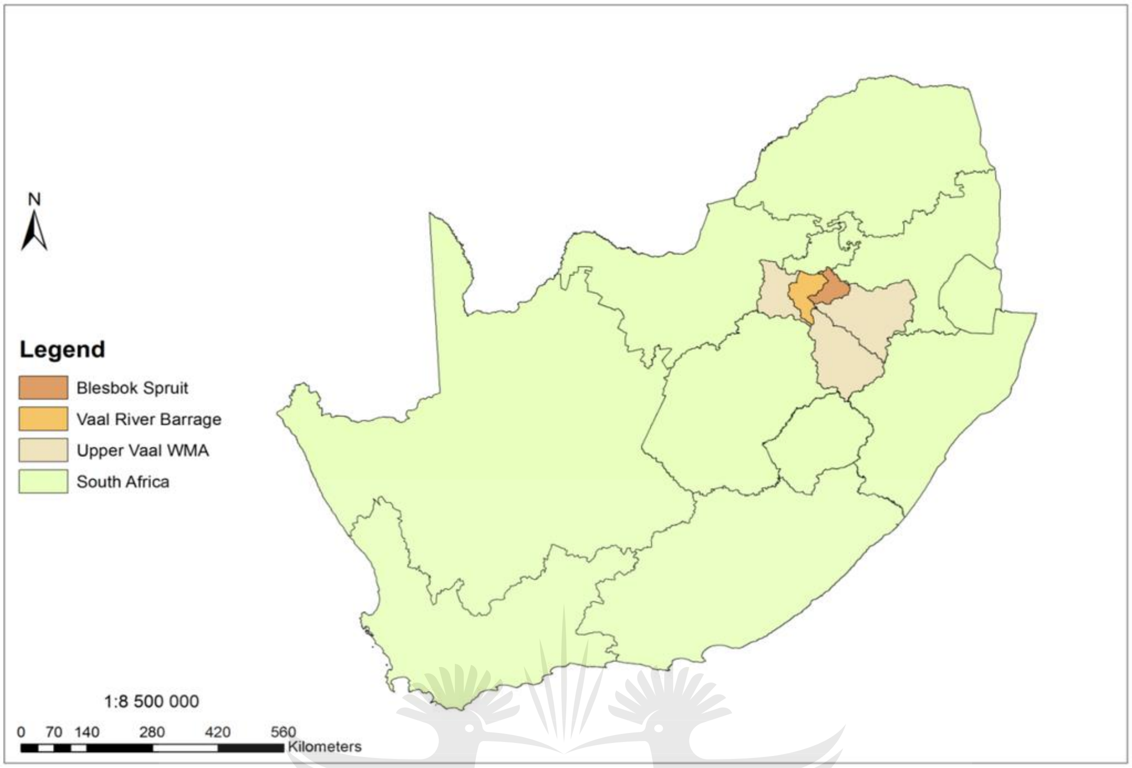

Figure 4. 1 Map of South Africa showing the Blesbokspruit water catchment (du Plessis *et al*., 2014)

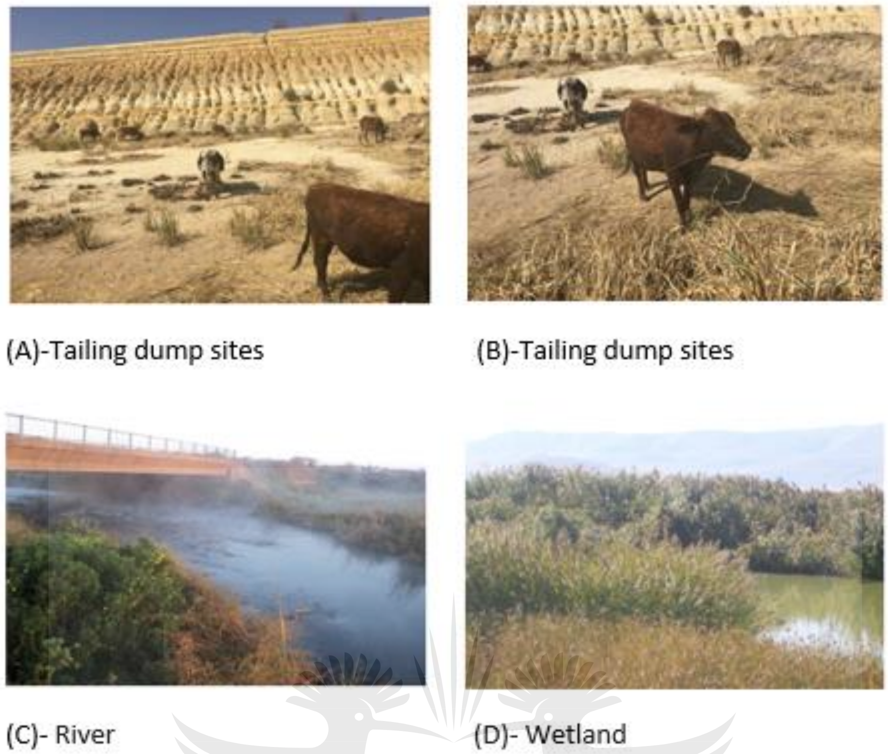

Figure 4. 2 Study area showing tailing dump site, wetland and river

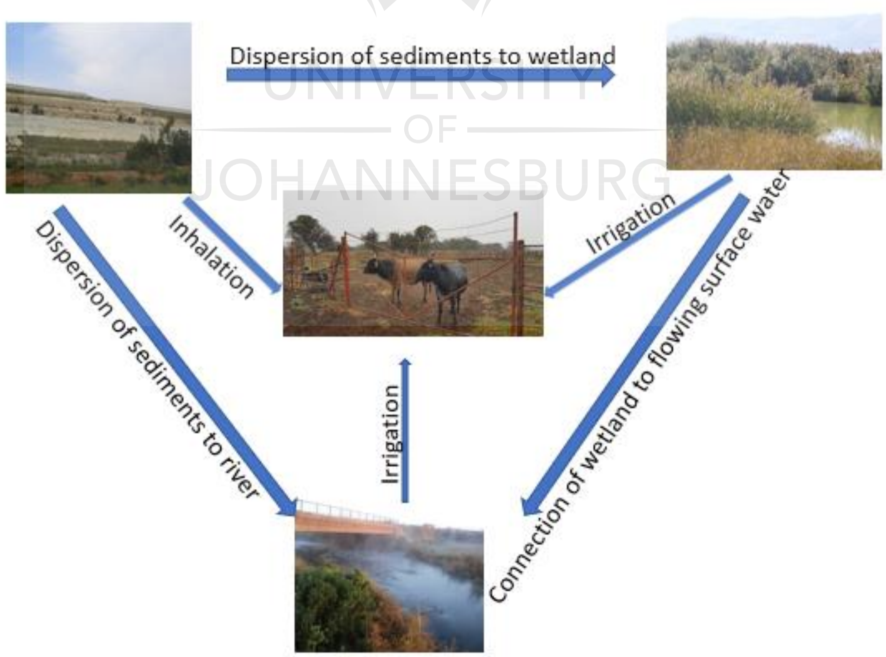

Figure 4. 3 Transfer mechanism of trace metals/elements

4.2.2 Collection of samples and pretreatment.

Using sterile bottles, water samples were randomly obtained from 4 sampling sites located at various directions and distances within the Blesbokspruit catchment. The water samples were assigned names; wetland (WL), Blesbokspruit (BS), Heidelberg (HB) and Suikerbosrand (SB). Soil samples (mine tailings sediments) - (MT) were collected using a Teflon-coated soil auger and put in labelled polyethylene bags with clear designation MT1 – MT4 respectively. The collected water samples from identified streams were stored in an insulated icebox and transported to the laboratory for storage at 4 ºC prior to further analysis. Collected soil samples were oven dried at 100 º C and then stored in polyethylene bags for mineralogical and trace metal analysis.

4.3 Analysis.

4.3.1 Experimental analysis.

Soil samples (tailings sediments) were oven dried at 100 ºC for 24 hours and mechanically passes through a sieve for particle distribution (ASTM, 2007). Approximately 2 g Aliquots of the various soil samples were weighed into a Teflon crucible, and then moistened with 100 mL of 1M HCl acid in a microwave digestion system for the determination of the HCl-soluble fraction of toxic metals. The mixtures were covered and placed on a shaker for 12 hours at 130 rpm. The solutions were filtered using a Whatmann filter paper, and the filtrates stored in sterile bottles prior to being analysed for potential toxic metals using inductively coupled plasma-optical emission spectrometry (ICP-OES, GBC Quantima Sequential).

At very high pressure using a mould, 10 g of each of the representative soil samples were pelletized, and then inserted in the sample compartment of an X-ray fluorescence (XRF; Rigaku ZSX PrismusII), to help in analysing the elemental compositions of the various minerals that make up the soil samples.

Morphological and mineralogical phase analysis of the tailing material were carried out using a scanning electron microscope (SEM, Tescan Vega 3 XMU) operated with an Oxford software and X-ray diffractometer (XRD; Rigaku Ultima IV) respectively.

In a soil-to-water suspension (1:2.5, w/w), the pH of representative soil samples was determined while electrical conductivity (EC) was measured in a 1:5 soil-to-water suspension using a Crison multimeter model MM 41. Also carried out was an assessment of the Total dissolved solids (TDS) in guidelines as stipulated by standard protocols of APHA (Clescerl *et al*., 1999).

4.3.2 Quality assurance and quality control.

For precision analysis, all reagents used were of analytical standards while apparatus, glassware inclusive were acid-washed with a 5 % nitric acid. Multiple levels of calibration standard solutions prepared from a Certipur ICP multi-element standard (Merck KGaA) by diluting the stock multi-elemental standard solution (1000 mg L^{-1}) in 0.5 % (v/v) nitric acid. The calibration curves for all the studied elements were in the range of 0.01 to 1.0 mg L^{-1}. The conditions of the ICP were the same as describe in a similar study as reported by Okereafor *et al* (Okereafor *et al*., 2019).

4.4 Results and discussion.

4.4.1 Particle size distribution of tailings sediments.

Table 4.1 highlights the textural characteristics of the tailings sediments as obtained from mechanical sieve analysis. The main fractions of all tailing sediments were fine sand (0.150 – 0.075 mm) and clay (0.075 - 0.053 mm) with average composition of 66.03 % for fine sand, 23.08 % clay and 10.89 % silt respectively. With fine sand constituting a major part of the soil within the tailing dump site which are loose with little or no vegetation cover, wind and soil erosion particularly during continued rainfall are likely to occur with no restriction. The steep and inclined nature of the dump will support surface run-off of sediments which end up as discharge into the wetland.

Table 4. 1 Sieve analysis of the soil from the gold mine tailing.

Sieve size (ASTM)	% Materials, Retains (gms)
No. 100	5.68
No. 140	45.51
No. 200	15.84
No. 270	10.25
PAN	22.72
Total	100
% Sand	67.03
% Silt	10.25
% Clay	22.72

4.4.2 Physicochemical analysis.

Various indices such as electrical conductivity, pH, moisture, soil organic matter, texture, temperature, etc. contributes to the quality of soil and as such have great influence on its basic functions such as water retention, promotion of biodiversity, flood resistance, landslides, erosion, agricultural support (Tale & Ingole, 2015). However, the physiochemical properties of water to a large extent affects water usage. **Table 4.2** gives a summary of the observed physiochemical properties of water analyzed in this study.

Table 4. 2 Physicochemical analysis of sediments and water samples

Sample Names	pH	EC µS/cm	TDS mg/L
Wetland (WL)	6.31	948.00	606.72
Blesbokspruit (BS)	6.33	1040.00	665.60
Heidelberg (HB)	6.34	1235.00	790.40
Suikerbosrang (SB)	6.35	488.00	312.32
Mine Tailing (MT)	4.21	132.00	84.48

4.4.2.1 pH of stream water and soil samples.

As a physical parameter, pH is a measure of the hydrogen ion concentration in the water/soil samples as ranked on a scale of 1.0 to 14.0. The lower the pH value of a material (soil/water), the more acidic it is and the higher the pH value, the basic, or alkaline, it is. Generally, many chemical and biological processes are affected by pH as different organisms flourishes better at different ranges of pH. A pH meter (Jenway model 3510) was used to determine the pH levels of the different water samples and sediments obtained from an abandoned golf mine dump. The observed pH values were within the limit of standard irrigation water (6.5 to 8.4), ranging from 6.31 – 6.35, thus validating the mobility and availability of toxic metals for plant uptake due to the presence of fewer H^+ ions (DWAF, 1996). A low pH of 4.21 was recorded for the tailings sediments which supports the heterogenous deposits of sulphidic residues from mining activities. The ability of plants to take up nutrients could be affected by the acidity of tailings, hence the sparse distribution of vegetation at the mine tailings site. The identified toxic metals (Zn^{2+}, Ni^{2+}, Pb^{2+}, AS^{2+}, Cu^{2+}) together with the observed pH of the tailings and wetland could result in Acid mine drainage (AMD).

In the long run, the continuous erosion of the tailings sediments to surrounding water bodies could result in damage to metal pipes, tanks and fittings used for irrigation purposes by farmers. Consequently, the alkalinity (acid absorbing potential) of the various water samples based on the reported pH (6.31 – 6.35) is an indication that most of the available dissolved carbondioxide have been converted into bicarbonate ion.

4.4.2.2 Electrical conductivity (EC).

The most influential water quality guideline on crop productivity is the water salinity hazard as measured by electrical conductivity (EC_w). EC measures salinity from all identified ions dissolved in a sample including negatively charged ions (e.g., Cl^-, NO^-_3) and positively charged ions (e.g., Ca^{++}, Na^+).

The values of electrical conductivity were determined by the concentration of ionic species contained in water. Using a standard of 84 µS and a Crison multimeter (MM 41), water samples from Heidelberg (HB) recorded the highest electrical conductivity value of 1235 µS followed by (BS) 1040 µS, (WL) 948 µS and (SB) 488 µS.

A value of 132 µS was recorded for the tailing sediments. The higher electrical conductivity (EC) recorded could imply the presence of higher dissolved salt or ion concentration which suggests that the samples have higher conductivity.

The observed high EC_w water on crop productivity will result in plants inability to compete with ions in the soil solution for water (physiological drought). The higher EC implies less water is available to plants, despite the soil appearing wet; thus, a reduced yield potential. This is because plants can only transpire "pure" water as usable plant water in soil solution decreases as EC increases.

4.4.2.3 Total dissolved solids (TDS).

Using the expression 0.64 x EC, a measure of the total dissolved amount of substance was obtained. The lowest value was observed in the (MT) 84.48 mg/L with (HB) recording the highest of 790.40 mg/L. (WL) and (BS) both had 606.72 mg/L and 665.60 mg/L respectively while 312.32 mg/L was recorded in (SB). Crop yield can be adversely affected by the higher concentration of salt in water thereby leading to soil degradation and pollution of ground water. This parameter however did not deviate from the international standards, but the high concentrations of dissolved solids could result in some technical effects. Dissolved solids can produce hard water, which leaves deposits and films on fixtures, and on the insides of irrigation pipes.

4.4.3 Chemical composition of tailings sediments.

The Energy Dispersive X-ray (EDX) microanalysis is a technique of elemental analysis associated to electron microscopy based on the generation of characteristic X-rays that reveals the presence of elements present in specimens. EDX technique is useful in the study of environmental pollution as it carries a huge vantage in the detection of toxic metals because they are nonbiodegradable and they can accumulate in ecological systems thus, resulting in pollution.

The Scanning Electron Microscope (SEM) and EDX (Energy Dispersive X-Ray Analyzer) analysis Fig. 4.4 indicate homogenous distribution of granules throughout mining tailing samples with EDX analysis, further confirming elements such as Si (33.58 %), Fe (19.12 %), O (54.25 %), Al (5.33 %), K (1.76 %), and Mg (0.44 %) which could be compared to elemental composition revealed from X-ray fluorescence (XRF).

A typical mineralogical composition of the tailings sediments is shown in Fig. 4.5 as determined by XRD. The XRD results confirm the presence of silicate minerals which are quartz (SiO_2), marcasite FeS_2, dialuminium silicate $Al(SiO_4)O$, pyrite (FeS_2) and gupeite (Fe_3Si). These could be linked with the elements identified from both XRF and ICP-OES.

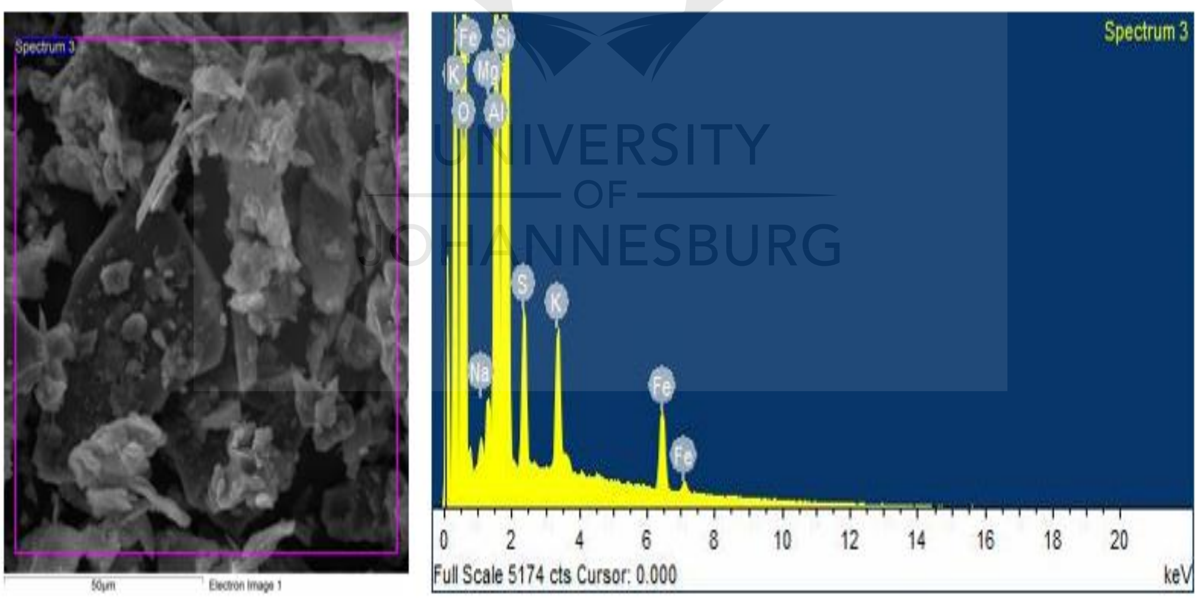

Figure 4. 4 SEM micrograph of tailings sediments.

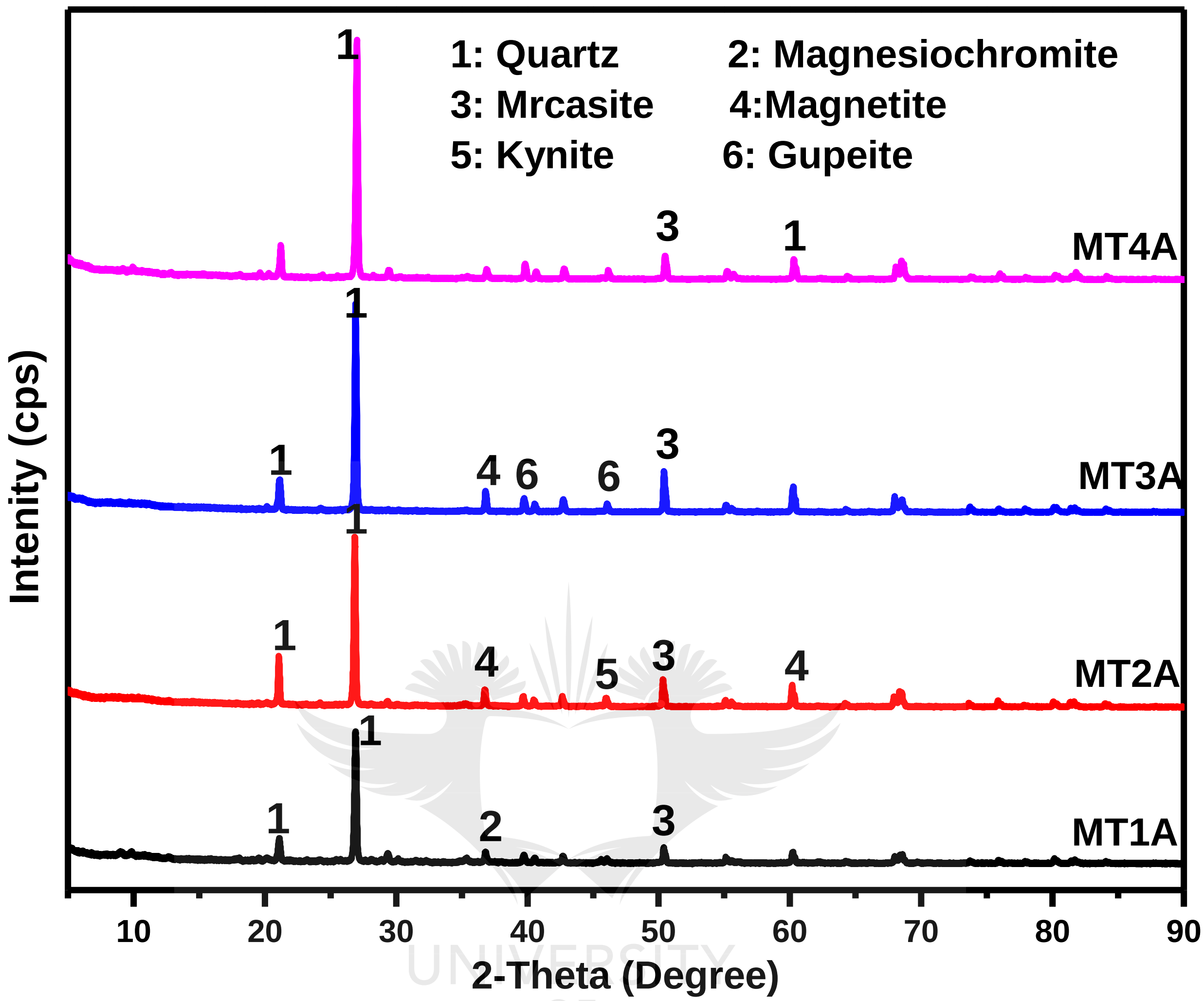

Figure 4. 5 XRD patterns of the filtered sediments.

Table 4.3 reports the partial compositional analysis of the tailing sediments collected from the abandoned gold mine dump. SiO_2 (81.82 %) was shown to be the most abundant compound found in the tailing sediments. The oxides of Al, Fe and S were 6.93 %, 3.59 % and 3.41 %, respectively. Oxides of K was 1.98 % while those of Na, Mg, Ca, Mn, Zn, Pb and Cu were less than 1 %.

Table 4. 3 Results of XRF Analysis detailing composition of tailing sediments.

Oxides	**MT1 Conc. (%)**	**MT2 Conc. (%)**	**MT3 Conc. (%)**	**MT4 Conc. (%)**	**$MT_{Ave.}$ Conc. (%)**
SiO_2	69.42	86.87	86.35	84.63	81.82
Al_2O_3	9.09	6.03	5.18	7.42	6.93
Fe_2O_3	5.87	2.37	2.60	3.53	3.59
SO_3	8.94	1.44	2.32	0.92	3.41
K_2O	2.71	1.61	1.64	1.96	1.98
MgO	1.49	0.38	0.30	0.33	0.63
TiO_2	0.58	0.49	0.51	0.49	0.52
CaO	0.90	0.23	0.55	0.13	0.45
Na_2O	0.27	0.14	0.14	0.16	0.18
Cr_2O_3	0.15	0.17	0.15	0.14	0.52
PbO	0.04	0.03	0.04	0.04	0.04
NiO	0.11	0.01	0.02	0.01	0.04

ICP-OES analysis as illustrated in Table 4.4 shows toxic metals concentrations in the sediments, wetland and surround streams. Filtrate from the tailing sediments showed very high concentration of various toxic metals with Cr recording the highest value of 43.13 mg/L, followed by Al 16.42 mg/L, As 10.17 mg/L, Pb 6.29 mg/L and Ni 1.34 mg/L respectively. Considering the proximity and the fact that the artificial wetland and studied streams all get fed from the run-off water from the dump site during rainfall, it is not a coincidence that higher metal concentrations were observed. Many metal elements are essential nutrients for animals and crops but, in excess, may result in chronic or toxic effects.

Table 4. 4 Results of ICP-OES Analysis on stream water samples and filtrate from tailing sediments showing mean toxic metal concentration.

Metal	**MT (mg/L)**	**WL (mg/L)**	**SB (mg/L)**	**HB (mg/L)**	**BS (mg/L)**	**DWAF (1990) Livestock**	**WHO (2011) Domestic**
Al	16.42	2.98	1.76	1.77	0.33	5.00	0.90
As	10.17	7.78	4.27	2.65	9.70	0.50	0.01
Cd	0.46	0.35	0.35	0.58	1.10	0.50	0.01
Pb	6.29	2.83	2.70	2.76	2.53	0.05	0.01
Ni	1.34	0.03	0.15	0.09	0.70	1.00	0.07
Zn	0.28	0.68	0.50	0.19	0.34	25.00	3.00
Cr	43.13	46.75	36.48	59.59	32.13	<0.05	<0.05
Cu	0.03	0.38	0.43	0.29	0.29	0.50	2.00

Toxic substances are often in solution or as suspended solids in water which may affect the nutritional availability of toxic elements or substance in animals. Although short-term intake of toxic substance by animals have little or no noticeable effects, long-term exposure to those substance may result in serious damage. The extent of damage inflicted on animals by toxic elements may be determined by health status, age and rate of consumption of toxic elements by the animals. However, the intake of toxic substances may not cause any measurable effect on growth, production, or reproduction, yet may cause sub-cellular damage in farm animals. This could be an expression of increased susceptibility to disease or parasitic invasion.

With agricultural activities taking place around the vicinity of the tailing dump, farmers employ water from the streams in irrigation and feeding of animals despite the high trace metal concentrations that apparently exceed the maximum permissible level of the United States Environmental Protection Agency water composition (Praveena *et al*., 2015; Dubey & Ujjania, 2015). Al, As, Zn, Cd, Ni, Cu, Pb and Cr were all above the required standard. There is a strong likelihood of the run-off water from the tailing dumps and fine particles being blown during severe windstorm introducing trace metals such as Al, As, Cd, Pb, Ni, Zn, Cr and Cu into nearby rivers.

Direct consumption of such waters by humans and animals such as cattle, gets into the gastro-intestinal system leaving some adverse effects by increasing the gastro-intestinal pH resulting in surficial coating on the stomach (Ekosse & Mulaba-Bafubiandi, 2008). In addition, some of the trace metals get leached into the water table through percolation and are absorbed by plants which the animals feed from.

In humans, several forms of cancer have been linked to arsenic, and chronic exposure to arsenic through drinking water has been associated to health effects such as nervous disorders, high blood pressure, diabetes, and hyperkeratosis (McDowell, 2003). However, there are little or no reports on the effect of arsenic in drinking water on the health and/or effect of farm animals. Arsenic availability in soil can disturb normal functioning of plant metabolism, consequently leading to stunted growth and low crop productivity (Nel *et al*., 2006). Previous studies indicated Arsenic to be responsible for reduction in gas exchange attributes (photosynthetic rate, transpiration rate, stomatal conductance) and chlorophyll concentrations (Anjum *et al*., 2017).

The total aluminium concentration in a human body is approximately 9 ppm (dry mass) with an approximately daily intake of 5 mg, of which only a small fraction is absorbed. The high aluminium content of the various water sources observed may have negative impacts on plants, humans and animals. Various ailments of the nervous system, such as Parkinson's disease, amyotrophic lateral sclerosis (Lou Gehrig's disease), and Alzheimer's disease as well as functional lung disorder may be experienced in humans (Krewski *et al*., 2007). There are currently no reports on Aluminium toxicity to ruminants. However, there are indications about the risks of inducing either a phosphorus deficiency or a condition known as grass tetany when ruminants consume large amounts of aluminium from soil, aluminium-rich forages or water high in aluminium content (Odette, 2005). In general, more soluble forms of aluminium in plants may pose some risk such as the inhibition of root elongation (Kochian *et al*., 2005).

Plant growth and development is often affected adversely by Cadmium a non-essential element due to its high toxicity and large solubility in water (Pinto *et al*., 2004). The uptake of minerals by plants have been reported to be altered by cadmium which impacts on the availability of minerals from the soil as well as a reduction in the population of soil microbes (Benavides *et al*., 2005).

Stomatal opening, transpiration, and photosynthesis have been reported to be affected by cadmium in nutrient solutions, but the metal is taken up into plants more readily from nutrient solutions than from soil (Sanita` di Toppi & Gabbrielli, 1999). The accumulation of cadmium in humans, could lead to renal failure, decreased vitamin D synthesis, and consequently osteoporosis. The high concentration of cadmium may adversely interfere with the metabolism of essential trace elements which in farm animals such as cattle could result in an unthrifty appearance, rough coat hair, dry scaly skin, dehydration, loss of hair from legs, thighs, ventral chest and brisket, mouth lesions, oedematous, shrunken scaly scrotum, sore and enlarged joints, impaired sight, extreme emaciation and some atrophy of hind limb muscles (Olobatoke & Mathuthu, 2016).

Despite plants being able to take up high levels of Lead of up to 500 ppm from soils, as toxic pollutants, Lead and some of its compounds can limit the synthesis of plant chlorophyll (Al-Akeel, 2016). The growth of plants is often retarded by higher concentrations of Lead. Crops cultivated in the study area stand a risk of suffering damage and reduced growth.

Besides gaining access into the food chain via plant uptake, humans through water intake, consume more lead. With the alarming concentrations of Lead shown in Table 4.4, inhabitants are likely to have excess lead intake which could, over time, result in paralysis, skin pigmentation and colic. Females may experience menstrual disorder, infertility and spontaneous abortion while children may suffer lower IQs, behavioural changes and concentration disorder. Lead is the most common cause of cattle poisoning. Animals die or perform poorly after inadvertently ingesting lead either through feed or water. Gradual poisoning of the areas cannot be ruled out as evidenced from the tailing sediments. Lead when consumed by ruminants end up in the reticulum (fore stomach) which provides a reservoir from which it is absorbed into the bodies of cattle, sheep and goats. In older cattle and sheep, subacute lead poisoning, is characterized by anorexia, rumen stasis, colic, dullness, and transient constipation, frequently followed by diarrhea, blindness, head pressing, bruxism, hyperesthesia, and incoordination (Cowan & Blakley, 2016).

Chromium (Cr) occurs in the environment primarily in two valence states, trivalent chromium (Cr III) and hexavalent chromium (Cr VI) with the latter being more toxic.

The high concentration levels of Cr as contained in **Table 4.4** is worrisome as it is known from previous studies to be a toxic metal that can cause severe harm to plants depending on its oxidation state. Some of the toxic effects of Cr on plants growth and development include alterations in the process of germination, growth of roots, stem and leaves, which may affect total dry matter production and yield (Bhalerao & Sharma, 2015). Excessive Cr also impact adversely on plant's physiological processes such as photosynthesis, water relations, mineral nutrition, oxidative imbalance and inhibition of enzymatic activities. Chromium can affect antioxidant metabolism in plant. The corrosive nature of some chromium (VI) compounds, when in excess result in ulcerations, dermatitis, and allergic skin reactions in humans. When inhaled on the other hand could lead to ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema (ATSDR, 2000). In mammals, chromium (III) is an essential trace element involved in lipid and glucose metabolism (DEFRA, 2002). Chromium VI as reported from previous studies adversely affected the developing embryo causing retarded fetal development in cattle during gestation resulting in reductions in the number of foetuses and fetal weight and a higher incidence of stillbirth and post-implantation loss (Pechova & Pavlata, 2007).

4.5. Conclusion.

This study revealed that the tailing sediments were largely comprised of fine sands that are loosely packed and prone to erosion thus supporting the migration of trace metal contaminants. The ability of plants to survive in the area based on the recorded physiochemical data such as acidity and electrical conductivity of the tailing sediments and water from wetland is daisy. A continuous erosion and surface run-off of sediments from the tailing dump site increases the migration of Al, As, Pb and Cr, which were observed to be in elevated concentrations, into the wetland and streams. Thus, endangering sustainable agricultural activities within the surrounding farmlands as water sources to farm facilities are highly prone to contamination from toxic metals trapped in tailing sediments especially given their high concentrations. The dispersion of such tailing sediments not only affects the agricultural activities within the studied area but may also have a health-related effect on the human population that reside in proximity to this mine dump. There should be metal speciation studies carried out to ascertain the extent of metal toxicity exposures within these areas.

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References.

Agency for Toxic Substances and Disease Registry (ATSDR). 2000. Toxicological profile for chromium. US department of Health and Human Services. Atlanta, US.

Alomary, A.A., Belhadj, S. 2007. Determination of heavy metals (Cd, Cr, Cu, Fe, Ni, Pb, Zn) by ICP-OES and their speciation in Algerian Mediterranean Sea sediments after a five-stage sequential extraction procedure. Environmental Monitoring and Assessment, 135: 265-280.

Al-Akeel, K. 2016. Lead Uptake, Accumulation and Effects on Plant Growth of common reed (Pharagmites Australis (Cav.) Trin. ex Steudel) plants in Hydroponic Culture. International Journal of Advances in Agricultural & Environmental Engineering, 3 (2), 391–394.

Anjum, S.A., Tanveer, M., Hussain, S., Ashraf, U., Khan, I., Wang, L. 2017. Alteration in Growth, Leaf Gas Exchange, and Photosynthetic Pigments of Maize Plants under Combined Cadmium and Arsenic Stress. Water Air Soil Pollution, 228, 13.

ASTM D422-63. 2007. Standard Test Method for Particle-Size Analysis of Soils.

Aznar-Sánchez, J.A., García-Gómez, J.J., Velasco-Muñoz, J.F., Carretero-Gómez, A. 2018. Mining Waste and Its Sustainable Management: Advances in Worldwide Research, Minerals, 8 (284), 1-27.

Benavides, M.P., Gallego, S.M., Tomaro, M.L. 2005. Cadmium toxicity in plants. Brazilian Journal of Plant Physiology, 17 (1), 21-34.

Bhalerao, S.A., Sharma, A.S. 2015. Chromium: As an Environmental Pollutant – A Review. International Journal on Current Microbiology and Applied Sciences; 4 (4), 732-746.

Calace, N., Di Muro, A., Nardi, E., Petronio, B., Pietroletti, M. 2002. Adsorption isotherms for describing heavy-metal retention in paper mill sludges, Industrial & Engineering Chemistry Research, 41, 5491-5497.

Clescerl, L., Greenberg, A., Eaton, A. 1999. Standard methods for the examination of water and wastewater. American Water Works Association Washington, DC. Part 3000.

Cowan, V., Blakley, B. 2016. Acute lead poisoning in western Canadian cattle — A 16-year retrospective study of diagnostic case records. Canadian Veterinary Journal; 57 (4), 421–426.

Department for Environment Food and Rural Affairs (DEFRA) and Environment Agency (EA). 2002. Contaminants in soil: Collation of toxicological data and intake values for humans. Chromium. R&D Publications TOX 4. Environment Agency. Bristol.

Department of Water Affairs and Forestry (DWAF). 1996. South African Water Quality Guidelines (second edition). Volume 4: Agricultural Use: Irrigation.

Dubey, M., Ujjania, N. 2015. Assessment of Water Quality and Sources of Pollution in Downstream of Ukai, Tapi River (Gujarat). Current World Environment, 10, 350.

du Plessis, A., Harmse, T., Ahmed, F. 2014. Quantifying and Predicting the Water Quality Associated with Land Cover Change: A Case Study of the Blesbok Spruit Catchment, South Africa. Water 6, 2946-2968.

Ekosse, G.I.E., Mulaba-Bafubiandi, A. 2008. Granulometric evaluation of continental bentonites and kaolin for ceramic applications. Journal of Applied Sciences, 8, 1021-1027.

Hudson-Edwards, K.A., Jamieson, H.E., Lottermoser, B.G. 2011. Mine wastes: past, present, future. Elements, 7, 375-380.

Jordan, G., D'Alessandro, M (eds). 2004. Mining, mining waste and related environmental issues: problems and solutions in Central and Eastern European Candidate Countries – Joint Research Centre of the European Commission, Ispra, EUR 20868 EN, ISBN 92-894-4935-7, 208.

Kochian, L.V., Pineros, M.A., Hoekenga, O.A. 2005. The physiology, genetics and molecular biology of plant aluminum resistance and toxicity. Plant Soil 274, 175–195.

Krewski, D., Yokel, R.A., Nieboer, E., Borchelt, D., Cohen, J., Harry, J., Kacew, S., Lindsay, J., Mahfouz, A.M., Rondeau, V. 2007. Human health risk assessment for aluminium, aluminium oxide, and aluminium hydroxide. Journal of Toxicology and Environmental Health, Part B, 10: 1-269.

Matinde, E., Simate, G.S., Ndlovu, S. 2018. Mining and metallurgical wastes: a review of recycling and re-use practices, Journal of the South African Institute of Mining and Metallurgy, 18 (8), 825-844.

McDowell, L.R. 2003. Minerals in Animal and Human Nutrition 2nd Edition, Elsevier, ISBN: 9780444513670, Gainesville, FL, USA.

McKinnon, E. 2002. The environmental effects of mining waste disposal at Lihir Gold Mine, Papua New Guinea, Journal of Rural and Remote Environmental Health 1 (2), 40-50.

Mineral and Petroleum Resources Development Act (MPRDA). 2002. Mineral and Petroleum Resources Development Act No. 28 of 2002.

Nel, A., Xia, T., Mädler, L., Li, N. 2006. Toxic potential of materials at the nano level. Science, 311, 622–627.

Nemati, K., Bakar, N.K.A., Abas, M.R.B., Sobhanzadeh, E., Low, K.H. 2011. Comparison of unmodified and modified BCR sequential extraction schemes for the fractionation of heavy metals in shrimp aquaculture sludge from Selangor, Malaysia, Environmental monitoring and assessment, 176, 313-320.

Obodo, G. 2004. The bioaccumulation of heavy metals in fish from Anambra River, Journal of Chemical Society of Nigeria, 29, 60-62.

Odette, O. 2005. Grass tetany in a herd of beef cows. Canadian Veterinary Journal; 46 (8), 732–734.

Okereafor, G.U., Mulaba-Bafubiandi, A.F., Mavumengwana, V. 2017. Possible heavy metals transportation and ground erosion during heavy rainfall in rural Mangweni (Tzaneen, Limpopo Province, South Africa). The Southern African Institute of Mining and Metallurgy, 515–522.

Okereafor, U., Makhatha, E., Mekuto, L., Mavumengwana, V. 2019. Dataset on Assessment of pollution level of selected trace metals in farming area within the proximity of a gold mine dump, Ekuhurleni, South Africa. Data in brief, 26: 104473. https://doi.org/10.1016/j.dib.2019.104473.

Olobatoke, R.Y., Mathuthu, M. 2016. Heavy metal concentration in soil in the tailing dam vicinity of an old gold mine in Johannesburg, South Africa. Canadian Journal of Soil Science. 96, 299-304.

Pechova, A., Pavlata, L. 2007. Chromium as an essential nutrient: A review. Veterinarni Medicina, 52 (1), 1-18

Pillay, K., Agjee, N.H., Pillay, S. 2014. Modeling changes in land cover patterns in Mtunzini, South Africa using Satellite Imagery. Journal of Indian Society of Remote Sensing, 42, 51–60.

Pinto, A.P., Mota, A.M., de Varennes, A., Pinto, F.C. 2004. Influence of organic matter on the uptake of cadmium, zinc, copper and iron by sorghum plants. Science of the Total

Environment, 326, 239–247.

Praveena, S.M., Yuswir, N.S., Aris, A.Z., Hashim, Z. 2015. Contamination assessment and potential human health risks of heavy metals in Klang urban soils: a preliminary study. Environmental Earth Sciences, 73, 8155-8165.

Puell, J.O. 2017. Methodology for a dump design optimization in large-scale open pit mines, Cogent Engineering, 4:1387955. https://doi.org/10.1080/23311916.2017.1387955.

Rahman, Z., Singh, V. 2016. Assessment of heavy metal contamination and Hg-resistant bacteria in surface water from different regions of Delhi, India. Saudi Journal of Biological Sciences, 25 (8), 1687-1695.

Sanita` di Toppi, L., Gabbrielli, R. 1999. Response to cadmium in higher plants. Environmental and Experimental Botany, 41, 105-130.

Sloss, L.L. 2017. Environmental and other effects of coal mining and transport, IEA Clean Coal Centre, ISBN: 978–92–9029–604–1.

Tale, K.S., Ingole, S. 2015. A Review on Role of Physico-Chemical Properties in Soil Quality, Chemical Science Review and Letters, 4 (13), 57 – 66.

Varol, M. 2011. Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. Journal of Hazardous Materials, 195, 355-364.

CHAPTER 5

RESULTS

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Assessing the effectiveness of *Hyparrhenia hirta* in the rehabilitation of the ecosystem of a gold mine dump.

5.0 Abstract.

The mining of gold is associated with several environmental challenges such as acid mine drainage, release of toxic metals which are associated to tailing sediments and have adversely impacted human health and the ecosystem. With increasing global population that is faced with limited land resources for agricultural activities, there is need for land restoration through effective rehabilitation of contaminated soils. The introduction of *Hyparrhenia hirta*, an indigenous grass specie as a phytoremediation technique for in situ rehabilitation of degraded soil is not only an economically viable approach but also environmentally friendly. *Hyparrhenia hirta* being a tufted and wiry perennial grass that is invasive with deep root system often aid in stabilizing the ecosystem owing to their self-fertile and drought resistant potentials that support that prevalence in harsh conditions at mine dump sites. In this study, mine tailings from an abandoned gold mine facility in Ekuhurleni, South Africa were assessed for trace metal contents at the same time analysing the uptake of such trace metals by *Hyparrhenia hirta* grass specie. The total metal mean concentrations was high (4023.67 mg/kg) for *Hyparrhenia hirta* which absorbed more of the following mean metal concentrations: 46.10 mg/kg for Cu; 40.08 mg/kg for Zn; 859.12 mg/kg for Pb; 618.26 mg/kg for Cr; 151.70 mg/kg for Co and 2308.41 mg/kg for Ni. The tailings were strongly acidic with a pH range of 3.86 – 4.34. These trace metals despite the acidic environments were successfully absorbed by *Hyparrhenia hirta* grass specie. Along these lines *Hyparrhenia hirta* was discovered reasonable for re-vegetation of mine tailings dump as it has the capacity to hold together tailings sediments against wind and water erosion.

Key words: Trace metals, Contamination, Plants, Mining, Ecosystem.

5.1 Introduction.

Globally, mine tailings which are usually waste products from the exploration and beneficiation of ores are on the increase and poses severe environmental hazards to both aquatic and terrestrial ecosystems due to improper management of mine tailings sites (Rashed, 2010). Tailings are mostly stockpiled above ground in containment areas or impoundments and often contain significant amount of several essential and non-essential metals. The concentration of metals such as As, Cd, Fe, Ni, Hg, Cu, Mn, Pb and Zn in mine tailings may range from as low as 1g/kg to greater than 50g/kg (Bradshaw *et al*., 1978; Aucamp & Schalkwyk, 2003; Nelushi *et al*., 2013; Fashola *et al*., 2016). At low concentration, non-essential metals are toxic whereas at higher concentrations essential metals are toxic (Frerot *et al*., 2006; Jaishankar *et al*., 2014).

Mine tailings are characterized by shales, cobbles, pebbles and sand sized particles, which have a very low water holding capacity and are low in nutrients such as nitrogen (N), Potash (K) and phosphorus (P) and organic matter required for biological growth and soil forming processes (Das & Maiti, 2007). Open dumping of mining waste and tailings deposits is a common practice in South Africa just like in other developing countries. It is noteworthy that the biotoxicity of mine tailings are supported by the presence of a low pH and metal content which increases the bioavailability of phytotoxic metal concentration (Stevenson & Cole, 1999; Ali *et al*., 2013).

Other features of tailings dump sites include the absence of topsoil, drought, surface mobility, periodic sheet erosion, compaction and absence of soil forming fine ingredients. Thus, the sparsely distribution of vegetation cover and a stressed heterotrophic microbial community at most mine tailings disposal sites (Mendez & Maier, 2008). These situations create in a sense the possibilities of having metal contaminants released during rain, resulting in metal leaching and the formation of acid mine drainages that adversely impact local streams and waterways (USEPA, 2004). Through food chain, several of these metals get transferred and accumulated in the bodies of animals or human beings, which have been reported from previous studies as responsible for DNA damage and carcinogenic effects due to their mutagenic abilities (Muhammad *et al*., 2011). Metal toxicity of mine tailings could negatively affect the number, diversity and activity of soil organisms and the inhibition of soil organic matter decomposition. Hence it is very crucial to effectively manage mine tailing wastes to curb the release of toxic metals into the environment.

Over the years, several methods such as physical removal (excavation), in situ stabilization of trace metals and the use of plants have been adopted in cleaning up the harmful effects of trace metals on contaminated sites. There are remarkable merits as well as demerits associated with each of the approaches whose success is largely dependent on the nature and size of the contaminated site. Indigenous native metallicolous plants due to their potentials for immobilization of trace metals based on documented evidences from studies are used in phytostabilization of metalliferous mine wastes (Conesa *et al*., 2007). They are often metal tolerant plant species with a high bio-concentration factor (metal concentration ratio of plant roots to soil) and low translocation factor (metal concentration ratio of plant shoots to roots).

Because of lack of competitors, these native plant species spread easily in these environments thereby increasing the heterotrophic microbial community, which may, in turn, promote plant growth and participate in metal stabilization (Glick, 2003; Weidenhamer & Callaway, 2010). Grasses are potential plant species for soil stabilization on account of their growth patterns and extensive rooting systems that are fibrous. Previous studies revealed that the roots of grasses slow soil erosion rates, support the formation of organic soil, conserve soil moisture and may compete with weedy species. As a perennial grass if managed properly, *Hyparrhenia Hirta* which is tufted, wiry and invasive grass specie, could be used productively to rehabilitate the ecosystem on a tailing dam. It occurs throughout Africa and in Pakistan, but a wider distribution is observed in southern Africa. It has upright flowering stems which are hairless with deep root systems.

Studies in Southern Spain reported *Lygeum spartum* L. (family Poaceae) to tolerate severe conditions of acidity pH of less than 5 (Conesa *et al*., 2007). According to various reports, *Vertiveria zizanioides* (Vetiver grass) is suitable for phytostabilization of mine tailings which is attributed to its tolerance to extreme soil conditions including prolonged drought, flood, a wide range of soil acidity, alkalinity, salinity, Al, Mn and toxic metals (As, Cd, Cr, Ni, Pb, Zn, Hg, Se and Cu) toxicities in the soil (Dalton *et al*., 1996).

In the United Kingdom, mine waste sites containing copper, lead and zinc were stabilized by grasses *Agrostis tenuis Sibthorp* and *Fistuca rubra* (Smith &Bradshaw, 1979; Bradshaw, 1997). Studies in China revealed plant species such as *Vetiveria zizanioides*, *Sesbania rostrata*, and *Leucaena leucocephala*, growing on Pb/Zn mine tailings dumps (Yang *et al*., 2003). Crops such as corn, maize and soybean were reported by (Zhou *et al*., 2002) as potential for Cu phytostabilization. The suitability of four Eucalyptus (E.) species (*E. cladocalyx, E. melliodora, E. polybractea*, and *E. viridis*) from the studies of (King *et al*., 2008) for the phytostabilisation of arsenical, sulphidic gold mine tailings revealed that *E. cladocalyx,* as an ideal candidate for the long-term phytostabilisation of As-contaminated land and mine tailings. The spread of toxic metals to crops and vegetables due to dust storms of less vegetated mine tailings as well as the contamination of streams by surrounding mine tailings dumps which poses great danger to the health of the residence of such informal settlements were reported in the studies of (Conesa *et al*., 2009).

Considering the importance to rehabilitate mine tailings dumps through the establishment of vegetative covers that can contain toxic metals by accumulation in their root tissues, leaves and stem; the aim of this study was to assess the concentrations of trace metals in soils and plants, and to put forward the potential of an indigenous grass *Hyparrhenia Hirta* as a suitable remediation strategy for the rehabilitation of selected abandoned gold mine tailings dumps in Ekuhurleni.

5.2 Materials and methods.

5.2.1 Study area.

The gold mine dump is in Blesbokspruit in Ekurhuleni metropolitan city of South Africa which lies on the southernmost part of the African continent, and characterized with varied topography, great natural beauty, and cultural diversity. The area is home to mild summers with temperatures seldom above 30° C. During spring and winter, northerly and north-westerly winds occur and during summer north-easterly to north-north-easterly winds occur (EMM, 2007). There are several seasonal pans across the area covering an area of about 3,559 hectares with a few lakes created by mines, which are used for recreational parks. Figure 5.1 detailed the location of the tailings dump while the specific description indicating coordinates of the sampling site within the dump are illustrated in **Table 5.1**.

Figure 5. 1 Location of sampling site.

Table 5. 1 GPS Co-ordinates of exact sampling location within the gold mine dump.

Station No.	Latitude (S)	Longitude (E)
1	$26^{0}\ 10'$	$28^{0}\ 27'$
2	$26^{0}\ 15'$	$28^{0}\ 35'$
3	$26^{0}\ 04'$	$28^{0}\ 40'$
4	$26^{0}\ 17'$	$28^{0}\ 44'$
5	$26^{0}\ 21'$	$28^{0}\ 50'$
6	$26^{0}\ 30'$	$29^{0}\ 10'$
7	$26^{0}\ 00'$	$29^{0}\ 15'$
8	$26^{0}\ 27'$	$29^{0}\ 20'$
9	$26^{0}\ 09'$	$29^{0}\ 35'$
10	$26^{0}\ 38'$	$29^{0}\ 42'$
11	$26^{0}\ 43'$	$29^{0}\ 47'$
12	$26^{0}\ 34'$	$29^{0}\ 50'$
13	$26^{0}\ 13'$	$29^{0}\ 53'$
14	$26^{0}\ 19'$	$30^{0}\ 10'$
15	$26^{0}\ 48'$	$30^{0}\ 15'$
16	$26^{0}\ 36'$	$30^{0}\ 25'$
17	$26^{0}\ 40'$	$30^{0}\ 29'$
18	$26^{0}\ 14'$	$30^{0}\ 35'$
19	$26^{0}\ 23'$	$30^{0}\ 40'$
20	$26^{0}\ 54'$	$30^{0}\ 48'$

5.2.2 Material description.

Attempt to assess the effectiveness of identified growing grass within the tailings dump as possible rehabilitation medium for toxic metal absorption, about 2 kilograms of 20 representative tailing samples as well as 20 grass samples were obtained from an abandoned gold mine dump. Preceding the removal of top tailing samples (2 cm) using an auger, samples were taken at a depth of 10 cm for every 50 m horizontal interval for a wider coverage. The collected soil samples (tailings) were kept cool in an icebox (< 4 ºC) and transported to the laboratory for further analyses in sterile plastic bags.

5.2.3 Experimental analysis for toxic metal content of mine tailings and grass samples.

Using 5 g each, 20 representative tailing samples were oven dried at 100 ºC for 24 hours, homogenized, and grounded to pass through a 2 mm sieve. The determination of the HCl-soluble fraction of toxic metals were carried out using aliquots of approximately 2 g of the various tailing samples weighed into a Teflon crucible and moistened with 100 mL of 1M HCl acid. The mixtures were covered and placed on a shaker for 12 hours at 130 rpm. The solutions were filtered through a Whatmann filter paper, and the filtrates were stored in sterile bottles prior to potential toxic metal analysis using inductively coupled plasma-optical emission spectrometry (ICP-OES).

Physicochemical properties such as pH and EC (electrical conductivity) of the tailings were measured in a soil-to-water suspension (1:2.5, w/w) and a 1:5 tailings-to-water suspension using a Crison multimeter (model MM 41) respectively (Aris *et al*., 2014). Loss on Ignition (LOI) analysis was used to determine the organic matter content (% OM) of the various tailing's samples (Robertson, 2011). The grain size distribution of tailing samples was determined using the hydrometer method (ASTM, 2007).

For precision analysis, apparatus and glassware used were acid-washed with 5% nitric acid while reagents were of analytical standards. Using ICP-OES (Model - GBC Quantima Sequential) operated under specific conditions of 1300W RF power, 15 L min^{-1} plasma flow, 2.0 L min^{-1}

auxiliary flow, 0.8 L min^{-1} nebulizer flow and 1.5 mL min^{-1} sample uptake rate, detectable toxic metals were determined. The calibration of the ICP-OES equipment was done by using multiple levels of calibration standard solutions prepared from a Certipur ICP multi-element standard (Merck KGaA). Potentially toxic metals such as Cu, Zn, Pb, Cr, Co and Ni determination were done using Axial view, while 2-point background correction and 3 replicates were employed in the measurement of analytical signal. The emission intensities were determined for the most sensitive lines free of spectral interference. By diluting the stock multi-elemental standard solution (1000 mg L^{-1}) in 0.5 % (v/v) nitric acid, the calibration standards were prepared. The calibration curves for all the studied elements were in the range of 0.01 to 1.0 mg L^{-1}. The bioaccumulation coefficient of the grass specie was carried out as described in previous study (Moreno-Jiménez *et al*.,2009).

5.2.4 Data analysis.

Trace metal concentrations of Cu, Zn, Pb, Cr, Co and Ni in ppm was obtained from the recorder output of Inductively Coupled Plasma-Optical Emission Spectrometer (model - GBC Quantima Sequential) which were then expressed in mg/kg. Data with replicates were presented as mean ±, standard deviation (SD).

5.3 Results.

5.3.1 Geochemical composition of gold mine tailings.

Tailings sediments from the gold mine dump exhibited an acidic pH within the range of 3.86 to 4.34 (**Table 5.2**). The reported acidity of the tailings could be attributed to high levels of sulphide and pyrite minerals which when exposed to oxygen and water result in acid mine drainage (AMD) (Bisht *et al*., 2016). From previous studies, the observed pH values are in line with typical pH value ranges of 2 to 4.4 usually found in acid mine drainage environments associated with gold and coal mining (Jennings *et al*., 2008). Agricultural activities may not be supported within the vicinity of the tailings dump on account of the level of acidity which may impair the uptake of major nutrients by plants. There is a likelihood based on the low CEC values for the soil not to hold enough water required by plants. The growing grass specie within the dump could be linked to the LOI which was in the range of (5.0 % - 5.4 %).

Table 5. 2 Geochemical compositions of gold mine dump.

	pH	C.E (mS/cm)	CEC (meq/100g)	LOI (%)
Mean	4.12	1.58	8.84	5.20
(SD)	0.22	0.04	0.11	0.02
Median	4.28	1.80	9.10	5.30
Min	3.86	1.30	8.30	5.00
Max	4.34	1.90	9.30	5.40
Mean, (Standard deviation), n = 20				

5.3.2 Trace metal distribution of tailings at gold mine dump.

The levels of trace metals such as Cu, Zn, Pb, Cr, Co and Ni were assessed at the gold mine dump (**Table 5.3**). Trace metals widely produce toxicity both in elemental and soluble salt forms as their presence in soils often distort important chemical processes in the ecosystem. The concentration of Cr [861.50 mg/kg] was the highest followed by Pb [123.70 mg/kg], Co [28.80 mg/kg] and Ni [25.40 mg/kg] respectively. The concentrations of both Zn [4.50 mg/kg] and Cu [0.20 mg/kg] were observed to be below 5 mg/kg. When compared with the South African soil background values; Pb, Cr and Co were seen to be 5.70, 11.98 and 1.60 times higher than the acceptable limits respectively (Herselman, 2007). Thus, the concentrations of these three metals in the tailings of the mine dump were significant above that of non-contaminated soils, revealing that the site was severely polluted with Pb, Cr and Co.

Soil contaminated with Pb disrupts the physical, chemical, and biological balance of soil systems. Previous studies reported severe health implications in inhabitants of mine areas in China as a result of pollution and soil contamination from Pb (Ogbonna *et al*., 2011). The accumulation of trace metals in soils dependent on their chemical form and intensity of rainfall result in devastating environmental challenges. This could be due to alterations in biological, chemical, and physical properties of agricultural soils (Ogbonna & Okeke, 2011). These trace metals are likely to find their way into the overall ecosystem via mechanisms such as food chain, surface and groundwater contamination via erosion.

Table 5. 3 Trace metal concentrations of tailings from gold mine dump (mg/kg).

	Cu	**Zn**	**Pb**	**Cr**	**Co**	**Ni**
Mean	0.20	4.50	123.70	861.50	28.80	25.40
(SD)	0.17	0.57	1.23	0.79	0.77	0.91
Median	0.10	5.20	123.55	860.45	28.20	25.45
Min	0.10	3.90	121.90	860.30	27.30	23.80
Max	0.60	5.60	125.80	862.60	30.20	26.80
Background Values	29.50	45.20	21.70	71.90	18.00	38.70

Mean, (Standard deviation), n = 20

5.3.3 Trace metal distribution of plant - *Hyparrhenia hirta* at gold mine tailings dump.

Metal toxicity from soils heavily contaminated with metals such as Mn. Cd, Cu, Pb and Zn adversely affect the quantity, diversity and activity of soil organisms; inhibits soil organic matter decomposition and reduces N-mineralization process (Rashed, 2010). In general, the normal trace metal levels of terrestrial plants cultivated in uncontaminated soils are in the range of 0.4 - 45.8 mg/kg for Cu, 1 – 160 mg/kg for Zn, 0.1 – 41.7 mg/kg for Pb, 0.006 – 18 mg/kg for Cr, 0.1 – 10 mg/kg for C0 and 0.4 – 3.7 mg/kg for Ni (Prasad, 2004).

The concentrations of metal in plants vary with the plant species as their uptake from soil occurs either passively with the mass flow of water into the roots, or through active transport across the plasma membrane of root epidermal cells. The bioavailability of trace metals to plants is governed by factors such as the nature of the soil, the total concentration of trace metal in the soil and their chemical forms (Hao & Jiang, 2015).

Unlike other mine dumps, *Hyparrhenia hirta* was the only specie of grass found growing around the site **Figure 5.2.** The concentrations of trace metals in the leaves of plants sampled in this study are presented in **Table 4**. The results indicate that the mean accumulated trace metals were found to be 46.10 mg/kg for Cu; 40.08 mg/kg for Zn; 859.12 mg/kg for Pb; 618.26 mg/kg for Cr; 151.70 mg/kg for Co and 2308.41 mg/kg for Ni.

Zinc is one of the most essential elements for plants but when compared with the concentrations of uncontaminated soil is low. This trend could be associated with the readiness with which it can be precipitated as the insoluble sulphate in the rhizosphere, thus preventing potential uptake and transport to the aerial parts of plants (Hao & Jiang, 2015).

The ability of *Hyparrhenia hirta* to survive in such acidic conditions and absorb these trace metals validate their usage for revegetation and stabilization of the tailings dump against wind and water erosion which supports the findings in previous study (Rashed, 2010).

Figure 5. 2 Grass specie (*Hyparrhenia hirta*) at the gold mine dump.

Table 5. 4 Trace metal uptake by Grass specie (*Hyparrhenia hirta*) at the gold mine dump (mg/kg).

	Cu	**Zn**	**Pb**	**Cr**	**Co**	**Ni**
Mean	46.1	40.1	859.1	618.3	151.7	2308.4
(SD)	0.5	0.5	5.1	2.8	0.8	0.5
Median	46.3	39.9	861.5	617.8	151.4	2308.4
Min	5.13	39.1	851.5	614.4	150.3	2307.5
Max	5.33	40.9	867.2	624.5	152.7	2309.6
Mean, (Standard deviation), n = 20						

5.3.4 Phytoaccumulation of trace metals and implications for phytoremediation.

Hyperaccumulators (plants) capable of striving in soils with very high concentrations of metals, absorbing such metals through their roots, and concentrating extremely high levels of metals in their tissues must exhibit a Biological accumulating coefficient (BAC) greater than 1 (Moreno-Jiménez *et al*., 2009). It is evident that *Hyparrhenia hirta* qualifies to be referred to as hyperaccumulator for trace metals Cu, Zn, Pb, Co and Ni. The findings from this study agree with those of (Moreno-Jiménez *et al*., 2009) in the phytoaccumulation of Cu and Ni metals in tailings from mine dumps. Both metals are possible hazards to both humans and animals and thus should be removed from the environment.

Considering the subsistence farming within the tailings dump site and the grazing of cattle as indicated in figure 5.2, there is a likelihood for trace metals to be transferred from the tailings to the grasses, cattle and subsequently humans.

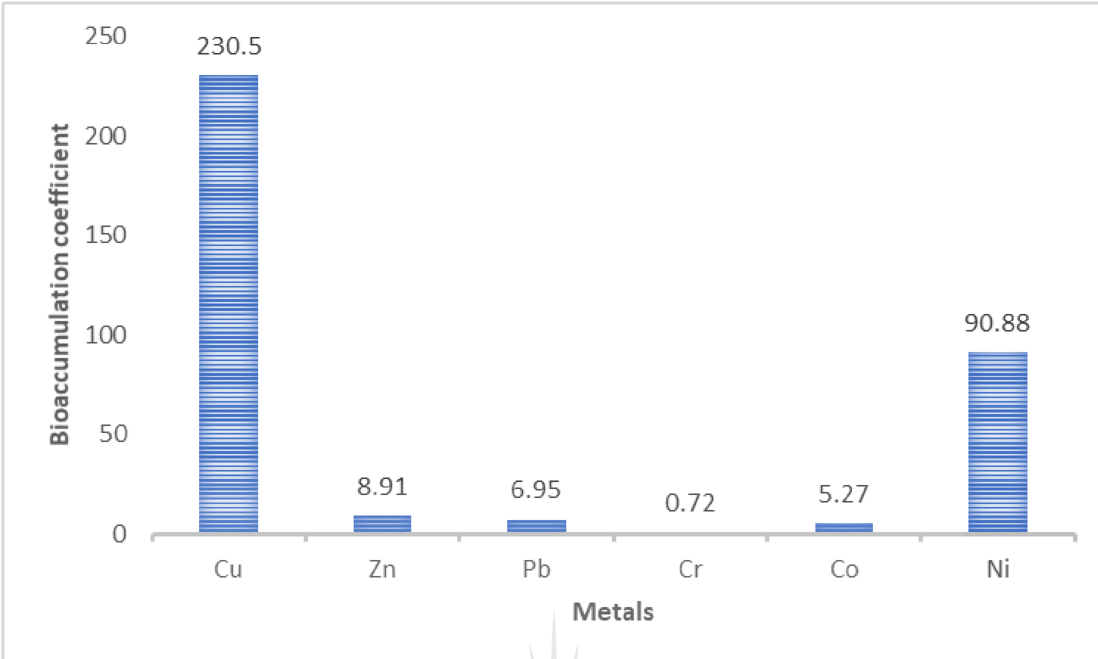

Figure 5. 3 The bioaccumulation coefficient (BAC = [metal] leave / [metal] tailings) for trace metals of *Hyparrhenia hirta* at the gold mine tailings dump.

5.4 Conclusion.

The study revealed that the gold mine tailings and grass - *Hyparrhenia hirta* contained trace metals mean concentrations, mg/kg, (Cu [0.20; 46.10], Zn [4.50; 40.08], Pb [123.70; 859.12], Cr [861.50; 618.26], Co [28.80; 151.70], Ni [25.40; 2308.41]) with alarming pH ranges of 3.86 – 4.34 and 5.13 – 5.33 respectively that poses danger to the immediate community and the environment. *Hyparrhenia hirta* found within the tailings dump may be qualified as an hyperaccumulator as it is suitable for rehabilitation of the tailings dump. However, the usage of *Hyparrhenia hirta* for the revegetation of the site may not be efficient due to the sparsely growth pattern observed leaving the area susceptible to soil erosion after heavy rainfall or windstorm, thus transporting tailings to nearby water sources.

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References.

Ali, H., Khan, E., Sajad, M.A. 2013. Phytoremediation of heavy metals-Concepts and applications, Chemosphere, 91 (7), 869–881.

Aris, A.Z., Ismail, F.A., Ng, H.Y., Praveena, S.M. 2014. Pertanika Journal of Science & Technology, 22 (2), 553–566.

ASTM International. 2007. ASTM D422-63 - Standard Test Method for Particle-Size Analysis of Soils, West Conshohocken, PA, USA.

Aucamp, P., Van Schalkwyk, A. 2003. Trace element pollution of soils by abandoned gold mine tailings near Potchefstroom, South Africa. Bulletin of Engineering Geology and the Environment, 62, 123-134.

Bisht, R., Agarwal, M., Singh, K. 2016. Heavy metal removal from wastewater using various adsorbents: a review. Journal of Water Reuse and Desalination, **7** (4), 387-419.

Bradshaw, A.D. 1997. Restoration of mined lands-using natural processes. Journal of Ecological Engineering, 8, 255-269.

Bradshaw, A.D., Humphreys, M.O., Johnson, M.S. 1978. The value of heavy metal tolerance in the revegetation of metalliferous mine wastes. In Goodman GT, Chadwick MJ, editors: *Environmental management of mineral wastes*, The Netherlands, 311-314.

Conesa, H.M., Schulin, R., Nowack, B. 2007. A Laboratory study on revegetation and metal uptake in native plant species from neutral mine tailings. Water Air Soil Pollution. 183 (1-4), 201-212.

Conesa, H.M., Moradi, A.B., Robinson, B.H., Kűhne, G., Lehmann, E., Schulin, R. 2009. Response of native grasses and *Cicer arietinum* to soil polluted with mining wastes:

Implications for the management of land adjacent to mine sites. Environmental and Experimental Botany, 65(2-3), 198-204.

Dalton, P.A., Smith, R.J., Truong, P.N.V. 1996. Vetiver grass hedges for erosion control on a cropped flood plain: hedge hydraulics. Agricultural Water Management, Elsevier, 31 (1-2), 91-104.

Das, M., Maiti, S.K., 2007. Metal mine waste and phytoremediation: A review. Asian Journal of Water, Environment and Pollution, 4 (1), 169-176.

Ekurhuleni Metropolitan Municipality. 2007. Ekurhuleni Metropolitan Municipality State of the Environmental Report 2007. www.ekurhuleni.gov.za [Accessed 1 July 2019].

Fashola, M.O., Ngole-Jeme, V.M., Babalola, O.O. 2016. Heavy Metal Pollution from Gold Mines: Environmental Effects and Bacterial Strategies for Resistance, International Journal of Environmental Research and Public Health, 13 (11), 1047.

Frerot, H., Lefebvre, C., Gruber, W., Collin, C., Dos Santos, A., Escarre, J. 2006. Specific interactions between local metallicolous plants improve the phytostabilization of mine soils. Plant and Soil, 282, 53-65.

Glick, B.R., 2003. Phytoremediation: synergistic use of plants and bacteria to clean up the environment. Biotechnology Advances, 21, 383-393.

Herselman, J.E. 2007. The concentration of selected trace metals in South African soils. Thesis (PhD - Soil Science), University of Stellenbosch.

Hao, Q., Jiang, C. 2015. Heavy metal concentrations in soils and plants in Rongxi Manganese Mine of Chongqing, Southwest of China. Acta Ecologica Sinica, 35, 46–51.

Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B.B., Beeregowda, K.N. 2014. Toxicity, mechanism and health effects of some heavy metals. Interdisciplinary toxicology, 7 (2), 60–72.

Jennings, S.R., Neuman, D.R., Blicker, P.S. 2008. Acid mine drainage and effects on fish health and ecology: a review. Bozeman: Reclamation Research Group Publication; 2008.

King, D.J., Doronila, A.I., Feenestra, C., Baker, A.J.M., Woodrow, I.E. 2008. Phytostabilisation of arsenical gold mine tailings using four Eucalyptus species: Growth, arsenic uptake and availability after five years. Science of the Total Environment, 406 (1–2), 35–42.

Mendez MO, Maier RM, Phytoremediation of mine tailings in temperate and arid environments. Reviews in Environmental Science and Biotechnology, 7 (1), 47–59.

Moreno-Jiménez, E., Peñalosa, J.M., Manzano, R., Carpena-Ruiz, R.O., Gamarra, R., Esteban, E. 2009. Heavy metals distribution in soils surrounding an abandoned mine in NW Madrid (Spain) and their transference to wild flora. Journal of Hazardous Materials, 15 (162), 854-859.

Muhammad, S., Shah, M.T., Khan, S. 2011. Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan, Microchemical Journal, 98, 334-343.

Nelushi, K., Gumbo, J. R., Dacosta, F. A. 2013. An investigation of the bioaccumulation of chromium and uranium metals by *Cynodon dactylon*: A case study of abandoned New Union Gold Mine Tailings, Limpopo, South Africa. African Journal of Biotechnology, 12, 6517-6525.

Ogbonna, P.C., Emea, R., Teixeira da Silva, J.A. 2011. Heavy metal concentration in soil and woody plants in a Quarry, Toxicological & Environmental Chemistry, 93 (5), 895 –

903.

Ogbonna, P.C., Okeke, V.I. 2011. Heavy metal level of soil and gmelina plantation in Umuahia, Nigeria. Terrestrial and Aquatic Environmental Toxicology, 5, 35–39.

Prasad, M.N.V. 2004. Heavy metal stress in plants: From Biomolecules to Ecosystems. Second edition, Norosa Publishing House, USA.

Rashed, M.N. 2010. Monitoring of contaminated toxic and heavy metals, from mine tailings through age accumulation, in soil and some wild plants at Southeast Egypt. Journal of Hazardous Materials, 178, 739-746.

Robertson, S. 2001. Direct estimation of organic matter by loss on ignition: methods. SFU Soil Science Lab. doi.org/10.1016/S1002–0160(11)60149–5.

Smith, R.A.H., Bradshaw, A.D. 1979. Stabilization of toxic mine wastes using tolerant plant populations, Transaction of the Institution of Mining and Metallurgy Section A. 81, 230-237.

Stevenson, F.J., Cole, M.A. 1999. Cycles of Soil (Carbon, Nitrogen Phosphorus Sulphur, Micronutrients). John Wiley and Sons Publishers, Hoboken, 427.

United States Environmental Protection Agency (USEPA). 2004. Abandoned mine lands team.

Weidenhamer, J.D., Callaway, R.M. 2010. Direct and indirect effects of invasive plants on soil chemistry and ecosystem function, J Chem Ecol., 36 (1), 59-69.

Yang, B., Shu, W.S., Ye, Z.H., Lan, C.Y., Wong, M.H. 2003. Growth and metal accumulation in vetiver and two Sesbania species on lead/zinc mine tailings. Chemosphere, 52: 1593-1600.

Zhou, L.B., Dai, H.W., Wu, Y.J., Gao, J.H., Ning, Y.P., Wang, Z.Y. 2002. Reclamation of copper mine tailings dams in Hujiaya using crops plantation. Mining Technology, 2

(2), 54-56.

CHAPTER 6

RESULTS

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Gold mine tailings: A potential source of silica sand for glassmaking.

6.0 Abstract.

Mining of minerals such as gold, copper, and platinum had been one of several activities sustaining the economy of South Africa. However, the mining sector has contributed significantly to environmental contamination through the improper disposal of mine tailings which covers vast areas of land. Therefore, this study utilized a vitrification process to manufacture glass from gold mine tailings. X-ray fluorescence was used to determine the chemical composition of the tailings while X-ray diffraction was adopted for the mineralogy. The tailings were of granitic composition enriched in potentially toxic elements such as copper, cadmium, zinc, lead, arsenic, and chromium. A representative sample of gold mine wastes of sandy grain size was used in making the glass. Based on composition, the glass was formulated by adding an average 10.0 mass% of $CaCO_3$ and 5.0 mass% of Na_2CO_3 to 35.0 mass% of SiO_2 which resulted in the production of a green-coloured glass.

Keywords: Silica sand, Beneficiation, Characterization, Gold mine tailings, Glass, Grain size.

6.1 Introduction.

Serious environmental risk are associated with mining wastes in a form of liquid and solid waste which contain potentially toxic elements such as cadmium (Cd), copper (Cu), zinc (Zn), lead (Pb), chromium (Cr), arsenic (As), and vanadium (V) (Krewski *et al*., 2007; Tchounwou *et al*., 2012; Ali *et al*., 2019). Among these environmental concerns includes the solubilization of sulphides from pyritic mine tailings which often results in acid mine drainages (Favas *et al*., 2016; Oyewo *et al*., 2018).

The Gauteng province of South Africa is characterized by numerous mine tailing dumps which are a result of previously active mining activities. Several decades of mining activities in the Gauteng Province of South Africa has had and continues to have a negative impact on ecosystems through the pollution of soils and water with high levels of potentially toxic metals such as As, Pb, and Al, as is the case with the old gold mine tailings in Blesbokspruit, Ekurhuleni South Africa (CSIR, 2013; Fashola *et al*., 2016; Olobatoke & Mathuthu, 2016; Singh *et al*., 2017). Previous studies have reported cases of health-related complications among dwellers who reside nearer to these mine tailing sites as a result of the contamination of agricultural soils, water sources, and atmospheric air by these mine tailings and effluents (Nelson *et al*., 2011; Plumlee & Morman, 2011; Momoh *et al*., 2013; Ngole-Jeme & Fantke, 2017; Entwistle et al., 2019; Ng *et al*., 2019; Okereafor *et al*., 2020).

Most gold mine tailings are composed mainly of industrial sand (i.e. silica) and silica sand is best described as a granular material that is composed of majorly quartz and trace amounts of coal, clay and other minerals (Beno *et al*., 2019). In some instances, it is referred to as either quartz or industrial sand and is widely applied in many engineering applications. When silica sand is present in metallic materials, it could serve as a source of crevice corrosion on such metals. Silica sand is mechanically and chemically purified quartz sand, from which various products are made using processes such as hydro classification and thermal treatments (Beno *et al*., 2019). The industrial application of silica sand is largely dependent on parameters such as the grain size, refractories, texture, and shape of the sample to be used (Malu *et al*., 2015). Over the years, silica sand has remained a vital component in various engineering projects and applications including building product and abrasive, glass making and hydraulic fracturing of oil wells (Malu *et al*., 2015; Beno *et al*., 2019).

The essential Silicon Dioxide (SiO_2) required for glass formulation is provided by silica sand, which makes silica the basic component in all forms of glass. Though the production of glass requires a variety of different materials, silica represents over 75 % of the final product (Hasanuzzaman *et al*., 2015). Silica is hard, chemically inert and has a high melting point, which could be linked to the strength of the bonds between the atoms. These are prized qualities in applications like foundries and filtration systems. Quartz is the most common silica crystal; it may be transparent to translucent and has a vitreous luster, hence it is used in glassmaking and ceramics. In 2003, South Africa based on silica as a mineral was reported to having 20 producers, 3 dormant mines, 2 decommissioned mines and 5 fume silica producers with most of the mining operations being in an opencast form (DME, 2004). The extracted silica sands are mostly from pegmatites, quartz massifs, veins or quartzites which are in the Western Cape, Mpumalanga and Gauteng regions (Edem *et al*., 2014). The United States of America recorded an increase in silica sand production between 1996 and 1997 from 2.5 to 28.5 metric tons of which 37 % was used in the manufacture of glass, 23 % as foundry sand, 6 % for hydraulic fracturing, and 5 % as abrasives (Garside, 2019). Continued usage of different forms of glass by individuals and organizations has necessitated an increasing global demand for the number of glass plants and industries (EC, 2007; Wintour, 2015; Wesgro, 2018).

As a waste disposal mechanism, the process of vitrification which involves the immobilization and encapsulation of radioactive and other types of hazardous materials at high temperatures (between 1100 ºC – 1600 ºC) result in such materials melting into a liquid which, on cooling, transforms to an amorphous, glass-like solid (Bingham & Hand, 2005). This process could be employed if the obtained glass is recycled in high-value applications (Binhussain *et al*., 2014). A herald of materials such as industrial wastes (Pe'rez *et al*., 1996), fly ashes (Haugsten & Gustavson, 2000), sewage sludge (Garcia-Valles *et al*., 2007) and pyrolyzed shales (Rangel *et al*., 2015) are involved in some of these applications. The usage of the afore-mentioned materials is advantageous in that they have undergone diverse industrial processes that leave them with good homogeneity and finer particle size. Also, the cost associated with the extraction of these materials is affordable as they are products of several initial processes.

The production of glass using gold mine tailings as a major raw material could help decrease the volume of waste exposed to atmospheric processes thus averting ecological pollution while at the same time, contributing to economic earnings. Reports from previous studies on the physicochemical composition of mine tailings generated during the extraction of gold show close features with those frequently used raw materials in glassmaking processes (Al-Harbi & Khan, 2009; Vatalis *et al*., 2014). The various environmental issues resulting from gold mine tailings had called for several scientific investigations to resolve the environmental burden that emanates from mine tailings. Some tailings dams have been partially or completely reclaimed leaving contaminated footprints. Some studies evaluated the potential to reuse mine tailings to produce bricks or ceramics (Ye *et al*., 2015; Kinnunen *et al*., 2018). In a recent study on gold tailings dam, It was found that the topsoil was highly acidified and only a minor portion of contaminants was bioavailable with the potential harm of phytotoxic contaminants such as Co, Ni, and Zn complicating rehabilitation measures as they limit the soil function (Rösner & van Schalkwyk, 2000). In addition, soil samples from this study area in a recent investigation revealed trace element concentrations, which often exceeded background concentrations in soils (Okereafor *et al*., 2019). Therefore, in a bid to extract value from gold mine tailings, this study was aimed at the quantification and qualification of gold mine tailings as a potential cheap silica source for the manufacture of glass.

6.2 Materials and methods.

6.2.1 Site description.

The study area (Figure 1.) is situated in the eastern region of the East Rand Basin within the Blesbokspruit catchment (26°10′12″S 28°27′52″E) in the Gauteng province, South Africa.

The materials used in this study included gold mine tailings (MT) that were logically collected from 4 different spots at an interval of 100 meters for a fair representation of the area. Each sample was separately and carefully collected using a disinfected auger to drill vertically downwards to a depth of 20 cm. This process was repeated at the different spots before transferring approximately 10 kg of each tailings material in labelled polyethylene bags designated MT1 – MT4 for purpose of identification. The tagged tailings samples were transported to the laboratory for preparation and further analysis.

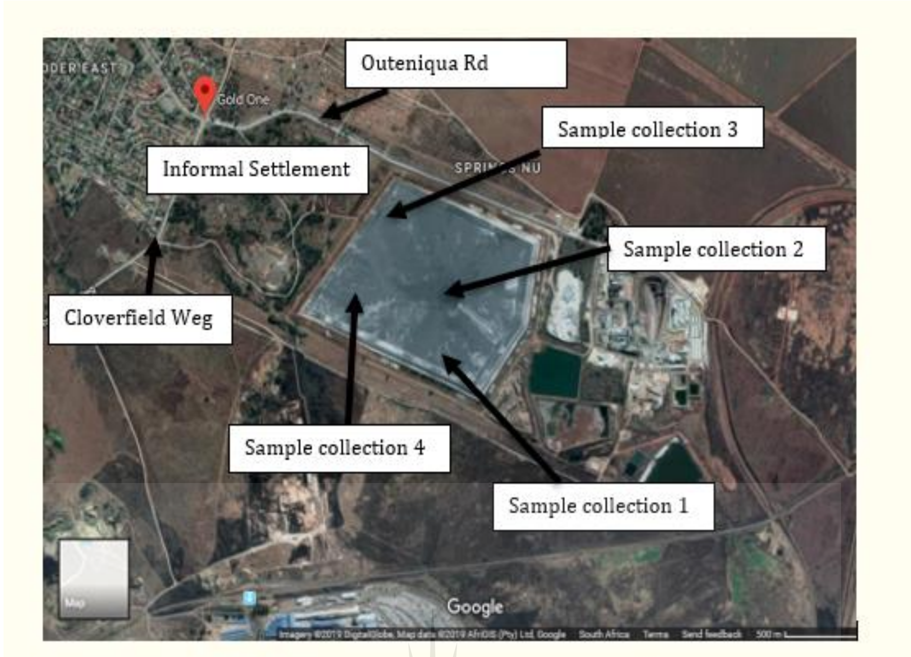

Figure 6. 1 Location of the sampling site 1cm to 500m.

6.2.2 Sieve analysis (Granulometric distribution).

Analysis of the grain-size of the silica sand from MT samples was determined using an electric sieving machine model (Filtra Vibracion SL – FTL 0200) operated under conditions of 230 V (50/60 Hz) 2A – 400 W with a standard set of sieves. This was done to provide information on the percentage ideal fraction of the sample. Two hundred and fifty (250) g of MT were weighed from each sample bag and thoroughly mixed in a pan for homogeneity to make a combined weight of one thousand (1000) g. The set of sieves utilized was in the range of (10 – 150 Mesh) which is equivalent to 2000 – 105 microns. 1000 g of as received gold tailings material was properly dried in an oven at 100 $^{\circ}$C for 30 mins to ensure easy separation. Arrangement of the set of sieves was in ascending order of Mesh number with the pan at the bottom for the collection of the finest particles. The dried sample was poured onto the sieve at the top (10 Mesh), covered with a lid, and carefully fixed onto the electric sieve shaker, and subsequently agitated for 15 minutes. Each sieve beginning from the top was removed and the retained grain size was poured on a clean white paper. A brush was used to ensure all sand particles retained in each sieve were removed onto the paper.

The weight of each collected grain size was determined using a Top pan balance model (Sartorius). The percentage retention of grain size was subsequently calculated (ASTM, 2007; Sundararajan *et al*., 2009).

6.2.3 Determination of moisture content and pH.

Using a clean crucible, 24.95 g of a composite MT was poured and weighed (W_1) using an analytical balance. With the aid of an oven operated at 105 ºC, the crucible containing the sample was heated for 1 hour after which the new weight (W_2) was checked. The difference between both weights was determined and expressed as a percentage.

$$\text{Moisture content} = \frac{W1 - W2}{W1} \text{ x } 100 \qquad \text{equation (1)}$$

The aim of measuring and controlling the moisture content of the samples is to ensure minimal casting defects that are associated with too much or too little organic materials within silica materials.

The pH of the samples was electronically determined using a Crison multimeter (model MM 41) of ± 0.1 percent sensitivity that was calibrated using a buffer solution (Aris *et al*., 2014). A representative sample of the tailings sediments was air-dried at room temperature for 6 hours. Afterward, using a chemical balance, 25 g of the dried sediments were weighed and poured into a clean beaker. This was done in triplicate. Subsequently, 40 mL of distilled water was added to each beaker using a volumetric cylinder. The solution was stirred with a glass rod and allowed to sit for 30 min. While waiting, Calibrate the pH meter was calibrated according to the manufacturer's instructions using two buffer solutions (pH 4.0 and pH 7.0). Before taking the pH readings of the sample, the mixtures were stirred again immediately. The precaution was taken not to place the electrode(s) directly in the sediment layer at the bottom of the beaker. Hence, the electrode(s) were positioned in the solution just above the sediment layer. After the initial reading (use), the electrode(s) were properly triple rinsed with distilled water before testing mixtures in beaker 2 and 3 respectively. The pH readings for the 3 mixtures were recorded to the nearest 0.1 pH unit and the average reported.

6.2.4 Determination of clay content.

About 2.465 kg of composite MT were introduced into a clean head pan containing water and the mixture thoroughly rubbed using bear hands. Decantation of the brown water from the mixture was done and repeated severally until a clear water colouration was observed in the mixture. The water was then decanted leaving behind wet sand which was air blown in a pressurized vacuum. The cake-like structure obtained was oven-dried at a temperature of 100 ºC for 3 hours (Edem *et al*., 2014). The dried sample was reweighed and expressed as a percentage.

$$\text{Percentage clay content} = \frac{m1-m2}{m1} \text{ x } 100 \qquad \text{equation (2)}$$

6.2.5 Grain morphology test.

The shape of silica sand is an important factor in the manufacture of glass products. Using an electronic microscope model (Olympus BX41), the shape of a composite MT was revealed to ascertain their suitability for glass production.

6.2.6 Specific gravity test.

With the aid of a specific gravity tester (model DH-300L), the specific gravity of a composite MT was directly obtained by introducing a very small sample into the equipment which automatically conducted the test and displayed the values digitally on a visual display unit.

6.2.7 Determination of metal oxides concentration.

X-ray fluorescence (XRF) using a Sequential X-ray Spectrophotometer (XRF; Rigaku ZSX PrismusII) was used in determining the chemical compositions of each MT. The spectrometer is calibrated by a set of more than 60 international standards. 10 g of each of the 4 collected pulverised MT samples was mixed with a selected binder (PVC dissolved in toluene) before being pelletized using a mould at very high pressure. The pellets were oven-dried at 50 ºC for 1 hour and subsequently placed in the sample compartment (Analyzer) of the spectrophotometer equipped with an end window 4 KW Rh-anode X-ray tube-powered at a voltage and current of 40 KV and 60 mA for heavy elements while light elements were at 30 KV and 100 mA respectively.

6.2.8 Determination of mineralogy.

Using approximately 5 g of oven-dried pulverized combination of the 4 collected representative MT samples, the XRD patterns were determined using a powder X-ray Diffractometer Model Rigaku Ultima IV with CuKα radiation (40 kV and 40 mA) having a scanning range of 4–100^o with a 0.017^o 2Ɵ step scan and a 50 s measuring time. The XRD aided the determination of the mineralogical composition of the material components and qualitative and quantitative phase analysis of multiphase mixtures. Individual reflection, as displayed by the X-ray diffraction, corresponded to a mineral. With peaks distinctly separated from each other, their heights were used to determine the orientation of identified minerals in the mixture. Mineral analysis of the gold tailings samples by X-ray diffraction was based on the identification of various peaks and by comparison of their relative heights. Respective phase levels were identified as semi-quantitative estimates based on their relative peak heights using a PAN analytical X'Pert High Score software. A wavelength of 1.5406 was employed in the calculation of the diffraction angles.

6.2.9 Removal of metals through leaching.

For best outcomes, 2 acids were utilized, nitric (HNO_3) and sulphuric (H_2SO_4) (Haghi *et al.*, 2016; Ko & Chu, 2018). In the first instance, 40 g of composite MT were weighed and poured into a 250 mL flask which was followed by the introduction of 100 mL of 1M nitric acid. The mixture was agitated at 850 rpm using a magnetic stirrer on a hot plate at a temperature of 80 ºC for 60 minutes. Evaporation was prevented during the process by placing a watch glass over the flask. The samples were filtered using a Whatman filter paper and the residue thoroughly washed using a solution of 10 % (2.5M) Sodium hydroxide (NaOH). The leaching process described above was repeated. This was to further remove potential residual impurities from the silica sand surface. A subsequent filtration of the mixture was done followed by drying of the residue in an oven for 3 hours (Veglio *et al.*, 1999; Tarasova *et al*., 2001). A similar process was repeated using 100 mL of 1M sulphuric acid and the percentage concentrations of metal oxides in each sample were evaluated using the procedure described earlier in **section 6.7**.

6.2.10 Qualification analysis as glass sand.

The qualification of extracted silica sand as potential glass sand was examined by making of actual glass using silica from composite MT. Glass products were made from extracted silica sand from composite raw MT, water treated MT obtained from section 2.4, and aid-treated samples from section 2.9 using $CaCO_3$ and Na_2CO_3 as fluxing agents. The mixtures were then heated in a muffle furnace at a temperature range of 1500 ºC – 1600 ºC for 2 hours. Four batches utilising each category of silica sand with a total mixture of 50 g in the ratio of 3:2:1 for silica, calcium carbonate, and sodium carbonate were used for the glass production. The mixtures were poured in 4 crucibles and carefully placed in the muffle furnace (Holand & Deubener, 2017). The role of the soda is to reduce the melting point of the silica sand, which in the long run will minimize energy consumption during manufacture. Unfortunately, Industrial practices have associated a drawback to the use of soda as it produces a kind of glass that would dissolve in water. However, the addition of limestone will mitigate the negative effect of soda (Bourhis, 2014). **Table 6.1**. below describe the batch compositions for glass production.

Table 6. 1 Batch composition for glass production

Sample code	Description	Silica (g)	$CaCO_3$ (g)	Na_2CO_3 (g)	Temp. (º C)
RT	Raw tailings	35.00	10.00	5.00	1520
WT	Water treated tailings	35.00	10.00	5.00	1520
$THNO_3$	Nitric acid treated tailings	35.00	10.00	5.00	1520
TH_2SO_4	Sulphuric acid treated tailings	35.00	10.00	5.00	1520

6.3 Results and discussions.

6.3.1 Physical analysis.

Table 6.2 presents a summary of some of the physical characteristic features of the MT. The percentage weight moisture content which is a combined loss of volatile matter such as structural water (H_2O) and carbon dioxide was observed to be 0.4 %. This moisture content value is an indication that the MT are suitable for use as silica for glass making due to the presence of moderate organic materials, hence the holding of little or no water within the silica system. This prevents the creation of gas defects in the final glass product (Edem *et al*., 2014).

A percentage of the clay content of 14.25 % was obtained after washing and drying the raw MT (**Figure 6.2**.). This is an indication that the grains are free of binders and will contain little or no water which could cause bubbles and defects.

The water-soluble level of alkalinity or acidity of the silica sand from the MT is revealed by the pH. A higher or lower pH indicates the presence of either acidic or basic oxides in each silica sand specimen which in this case was found to be 4.28. This value is close to neutral (7.00) and could be used for glass making (Anaekwe & Hassan, 2017).

The specific gravity value of 2.50 obtained in the analysis is an indication that the silica sand from MT is suitable for glassmaking since values above 2.65 are considered not suitable (Duvuna & Ayuba, 2015).

Table 6. 2 Physical analysis of silica sand from MT.

Property	**Silica sand (MT)**
Moisture content (%) at 105 ºC	0.40
Clay content (%)	14.25
pH	4.28
Grain shape	Subangular
Specific gravity	2.50
Appearance (colour)	Grey to light brown colouration.

Figure 6. 2 Water treated silica sand from MT (Scale: 4.86 cm x 13.02 cm).

6.3.2 Granulometric analysis.

Table 6.3 illustrates the grain size distribution of the MT materials. The result revealed that the highest percentage retention fraction of the silica sand from the MT samples was within mesh number 53 – 100 (96 %). Large grain particles partially mix with other grains in a batch while air bubbles are created in the final glass product by fine grain. The size analysis conducted thus far indicated that the silica sand met the prescribed standard range of over 90 % of particle size within the 15 – 100 mesh (BS sieve number) (Pisutti *et al.*, 2008).

Table 6. 3 Grain size distribution analysis of MT samples.

Mesh No.	**Serial number**	**Weight of particle (g)**	**% Composition**
10	223257	11.72	1.17
53	701184	951.61	95.16
75	700749	9.34	0.93
106	700774	7.65	0.77
150	701185	3.99	0.40
Pan	Nil	8.90	0.89

6.3.3 Concentrations of metal oxides.

The percentage of chemical compositions of the MT is presented in **Table 6.4**. The result revealed SiO_2 as having the highest percentage composition in the sample with a value of (88.72 %) followed by Al_2O_3 (4.44 %), K_2O (1.55 %), Fe_2O_3 (1.42 %), TiO_2 (0.42 %), MgO (0.27 %), CaO (0.22 %), and smaller amount of other oxides such as Na_2O, NiO, ZnO, BaO, CuO, MnO, and PbO. The high percentage of SiO_2 in the tailings material is an indication of the presence of silica sand which is similar to the findings from previous studies (BS, 1988; Tabelin *et al.*, 2009; Babasaheb, 2010; Tomiyama *et al.*, 2019). Upon comparison of the observed percentage compositions of the gold tailings from this study with the International minimum standard of silica sand used for glass making (**Table 6.5.**), it was evident that the concentration of SiO_2 (88.72 %)

was below the required threshold which could be attributed to some mechanical and geological factors, CaO + MgO falls within the minimum standard while those of Al_2O_3, Fe_2O_3, and TiO_2 were above the stipulated standard. The concentration of Fe_2O_3 in any silica sand used for glass production determines the colour of such glass as a slight increase could result in a green, yellow or red colouration. In certain situations, the colouration is neutralized by the introduction of manganese resulting in a faint shade of purple colour (Heck & Hoffmann, 2002). Edem *et al* (2014) while using Silica sand deposits from a riverbed observed that a lower concentration of Fe_2O_3 resulted in the formation of a Tableware and lead crystal glass (Edem *et al*., 2014). In contrast with de Melo et al (2012), a homogeneous shiny dark brown-coloured glass composed of 40.0 wt. (%) of sandy tailing and 60 wt. (%) of steelwork slag was observed (de Melo *et al*, 2012). The high percentage of iron oxide is an indication that the silica sand is suitable for coloured and insulated glass as the iron content is above 1 %. The high alumina also supports the tensile strength and stability of the glass. The MT require beneficiation to reduce the level of iron, titanium, and aluminium as a way of increasing the number of areas for its utilization in the glass industry. The high concentration of K_2O could be beneficial in increasing the refractive index of potential glass products (Hubert, 2015).

Table 6. 4 Result of chemical analysis of 4 representative MT samples.

Sample	SiO_2 (wt.%)	TiO_2 (wt.%)	Al_2O_3 (wt.%)	Fe_2O_3 (wt.%)	MnO (wt.%)	MgO (wt.%)	CaO (wt.%)	Na_2O (wt.%)	K_2O (wt.%)	P_2O_5 (wt.%)	Pb (mg/kg)	Zn (mg/kg)	Cu (mg/kg)
MT1	89.03	0.44	4.43	1.42	0.04	0.26	0.21	0.17	1.53	0.06	300	500	100
MT2	88.87	0.41	4.33	1.37	0.03	0.28	0.21	0.14	1.57	0.07	200	700	200
MT3	88.35	0.43	4.48	1.41	0.03	0.25	0.20	0.14	1.54	0.05	300	400	200
MT4	88.63	0.40	4.52	1.48	0.02	0.29	0.26	0.16	1.56	0.05	400	700	300
MT_{AVE}.	88.72	0.42	4.44	1.42	0.03	0.27	0.22	0.15	1.55	0.05	300	500	200

Table 6. 5 General specification of the chemical composition of silica sand for glassmaking (Pisutti et al., 2008; GWP, 2010).

Glass type	Grade	SiO_2 %	Fe_2O_3 %	Al_2O_3 %	CaO + MgO %	TiO_2 %
Optical and ophthalmic glass	A	99.800	0.013	0.200	0.100	0.000
Tableware and lead crystal glass	B	99.600	0.050	0.500	0.200	0.012
Borosilicate glass	C	98.500	0.150	0.500	0.500	0.100
Colourless container ("flint")	D	95.000	0.200	4.000	0.500	0.100
Clear flat glass	E	95.000	0.300	0.500	0.500	0.100
Coloured container glass	F	95.000	1.000	4.000	0.500	0.100
Insulating fibres	G	94.500	1.000	4.000	0.500	0.100

6.3.4 Mineralogy.

Table 6.6 and **Figure 6.3** each illustrates the principal minerals present in the silica sand from MT samples. The result reveals various principal minerals such as Quartz, Magnesioferrite, Marcasite, Magnetite, Kyanite, and Gupeite as present in the MT. Quartz in the form of silica (SiO_2) was the predominant mineral in the tailings which based on its abundance, crystalline nature, high thermal, and chemical properties, could be utilized in many large-scale applications. With quartz as the dominating mineral, the silica sand from the MT could be considered for manufacture of container glass, flat plate glass, specialty glass, and fiberglass on account of its luster, colour, and diaphaneity.

Table 6. 6 Principal minerals in silica sand from MT.

Mineral present	Chemical composition
Quartz	SiO_2
Magnesioferrite	$MgO.O_6FeO_{94}$
Marcasite	FeS_2
Magnetite	Fe_3O_4
Kyanite	$Al_2(SiO_4)O$
Gupeite	Fe_3Si

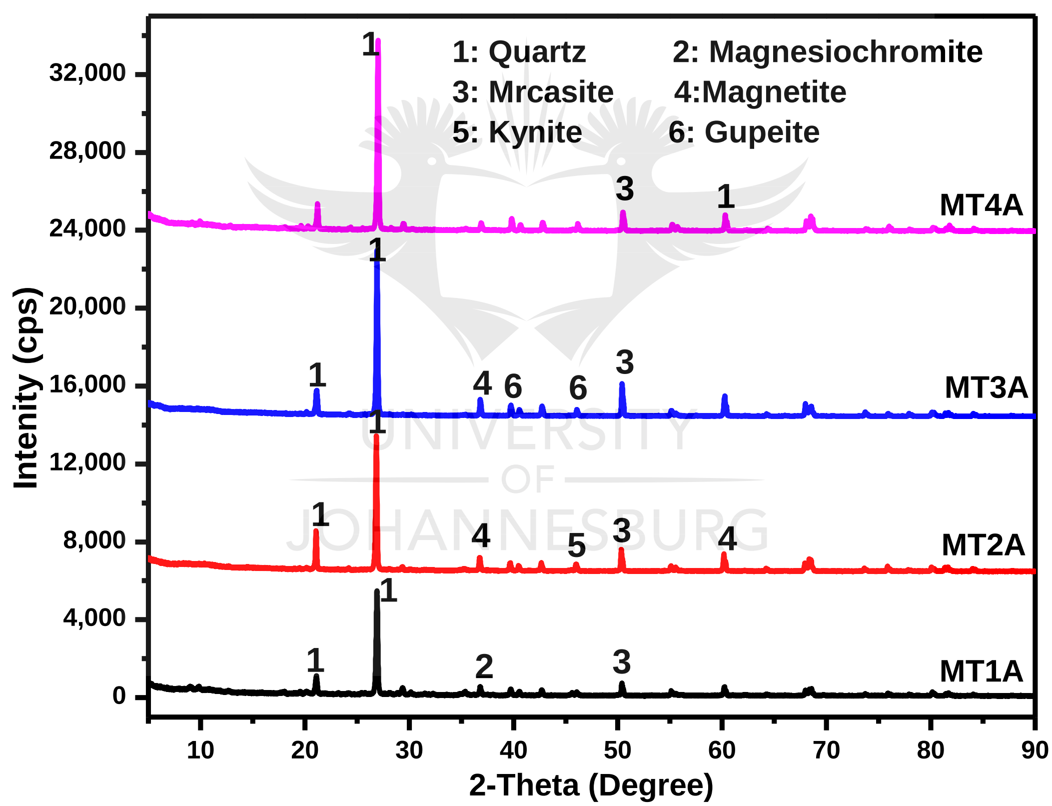

Figure 6. 3 XRD patterns of silica sand from MT (Scale: 10.96 cm x 15.48 cm).

6.3.5 Beneficiation of silica sand from MT.

After a physical separation technique using water and acid leaching of the materials as described in sections 6.2.4, 6.2.7, and 6.2.9 respectively, there was an appreciable increase in the silica content with a corresponding reduction in impurities such as iron oxide, alumina, titanium oxide, and potassium oxide respectively. A summary of the chemical composition of the treated silica sand is described in **Table 6.7.**

Table 6. 7 Summary of the chemical composition of the extracted treated silica sand

Sample	**SiO_2 (wt.%)**	**TiO_2 (wt.%)**	**Al_2O_3 (wt.%)**	**Fe_2O_3 (wt.%)**	**MnO (wt.%)**	**MgO (wt.%)**	**CaO (wt.%)**	**Na_2O (wt.%)**	**K_2O (wt.%)**	**P_2O_5 (wt.%)**	**Pb (mg/kg)**	**Zn (mg/kg)**	**Cu (mg/kg)**
A	88.72	0.42	4.44	1.42	0.03	0.27	0.22	0.15	1.55	0.05	300	500	200
B	88.81	0.40	4.41	1.38	0.01	0.25	0.20	0.13	1.48	0.04	260	400	150
C	89.53	0.33	2.31	1.31	0.01	0.18	0.18	0.10	1.17	0.02	200	300	-
D	89.82	0.31	2.19	1.27	0.01	0.15	0.15	0.09	1.03	0.01	200	100	-

NB: A = Raw Tailings, B = Water treated tailings, C = HNO_3 treated tailings, D = H_2SO_4 treated tailings

6.3.6 Qualification analysis.

The production of low melting glass was observed at a temperature of 1520 ºC after 2 hours. The mixtures resulted in various glassy phase samples. The glassy material was not fully liquidized at this temperature and time, hence could not be poured onto a mould. Upon cooling, the crucibles were carefully broken using a hammer to expose the final products as shown in **Figure 6.4**. Glassy phase formations from batch compositions (B) and (D) had noticeable green colouration which could be linked to the iron content of the silica sand used. With batch compositions (A) and (C), there were whitish structures that could be due to the refining process.

The materials from batch (D) demonstrated the highest quality of glass which supports the industrial requirements as described in Table 6.5 and a previous study (Afonso *et al*., 2016). Batch (D) just like in a commercial glass plant, will have to be subjected to further processing by including waste glass (from recycling collections), and heated in a furnace. The green colour provided by iron oxide, could be neutralized by adding other metal oxides such as Zinc oxide to the molten glass to produce a white product (Lockhart, 2006).

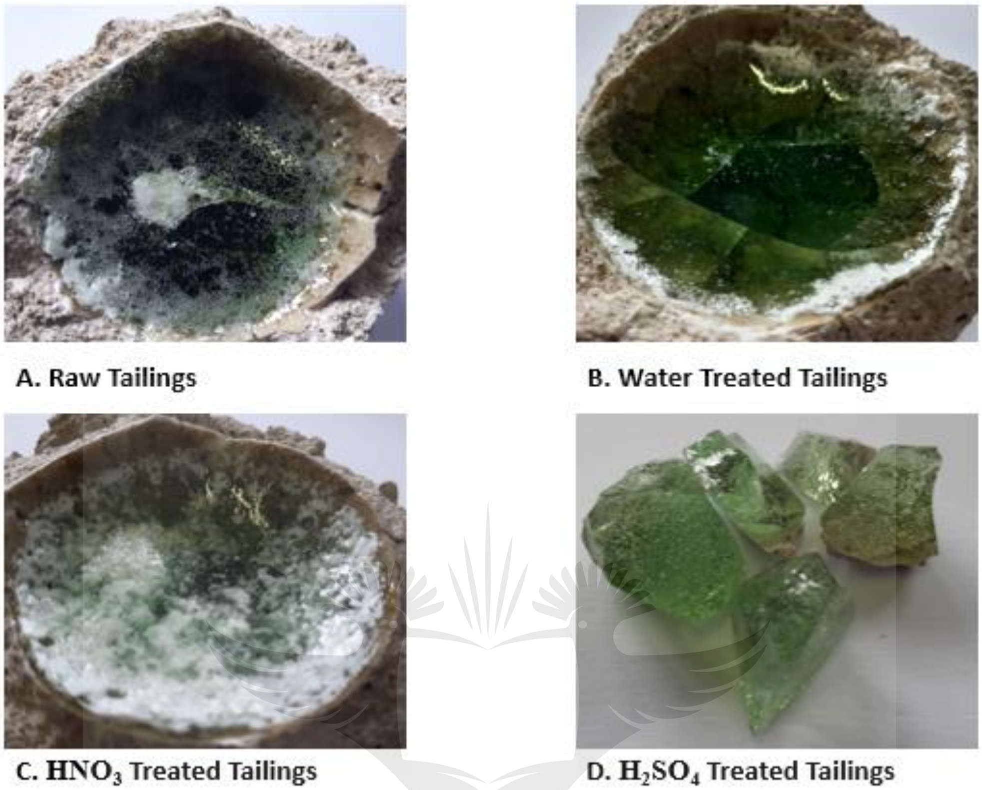

Figure 6. 4 Glass samples produced from the various batch compositions.

6.4 Conclusion.

For the first time, this study investigated MT as a source of silica in glassmaking to mitigate the negative environmental burden that these tailings possess. Based on the high percentage of silica in these mine tailings, which is a major constituent and other physical attributes such as grain size and morphology that met the requirements for glassmaking, the MT from this study could be a cheap and readily available source of silica sand for the glass manufacturing industry. Raw, water-treated, nitric acid-treated, and sulfuric acid-treated MT were tested to ascertain the quality of the glass material produced. Based on the observed qualification tests, the sulfuric acid-treated tailings produced a satisfactory green glass quality while raw, water-treated and nitric acid-treated tailings showed white residues that reduce the quality of the glass. It is recommended that further beneficiation towards reducing the iron oxide on sulphuric acid-treated gold tailings be carried out to widen the application to other forms of glass and not limited to green-coloured and amber glass production.

Author Contributions.

Conceptualization, M.M. and V.M.; methodology, U.O.; software, L.M.; validation, U.O., L.M. and V.M.; formal analysis, U.O.; investigation, U.O.; resources, M.M.; data curation, U.O.; writing—original draft preparation, U.O.; writing—review and editing, L.M. and V.M.; visualization, U.O.; supervision, M.M.; project administration, L.M. All authors have read and agreed to the published version of the manuscript.

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References.

Al-Harbi, O.A., Khan, M.M. 2009. Utilization of Local Raw Materials for the Production of Commercial Glasses. Trends in Applied Sciences Research. 4 (4), 176 - 187.

Alfonso, P., Castro, D., Garcia-Valles, M., Tarrago, M., Tomasa, O., Martınez, S. 2016. Recycling of tailings from the Barruecopardo tungsten deposit for the production of glass. Journal of Thermal Analysis and Calorimetry. 125, 681–687.

Ali, H., Khan, E., Ilahi, I. 2019. Environmental Chemistry and Ecotoxicology of Hazardous Heavy Metals: Environmental Persistence, Toxicity, and Bioaccumulation. Journal of Chemistry. Article ID :6730305.

Anaekwe, N.O., Hassan, Y.M. 2017. Chemical evaluation of the glass making potentials of silica sand deposits along Cross river in Cross River State, South-East of Nigeria. European Journal of Engineering Research and Science. 2 (6), 12 - 17

Aris, A.Z., Ismail, F.A., Ng, H.Y., Praveena, S.M. 2014. An Experimental and Modelling Study of Selected Heavy Metals Removal from Aqueous Solution Using Scyllaserrataas Biosorbent. Pertanika Journal of Science & Technology. 22 (2), 553 - 566.

American Society for Testing and Materials (ASTM). 2007. D422-63. Standard Test Method for Particle-Size Analysis of Soils.

Babasaheb, A.B. 2010. Geological exploration of friable quartzite (glass sand) deposit of Jiajuri District (phase I and II). Nagpur: Nagaon, Assam Mineral Exploration Cooperation. 1 - 8.

Beňo, J., Adamusová, K., Merta, V., Bajer, T. 2019. Influence of Silica Sand on Surface Casting Quality. Archives of Foundry Engineering. 19 (2), 5 - 8.

Bingham, P.A., Hand, R.J. 2005. Vitrified metal finishing wastes: I. Composition, density and chemical durability. Journal of Hazardous Materials. 119, 125 – 133.

Binhussain, M.A., Marangoni, M., Bernardo, E., Colombo, P. 2014. Sintered and glazed glass-ceramics from natural and waste raw materials. Ceramics International. 40, 3543 – 3551.

Bourhis, E.L. 2014. Glass: Mechanics and Technology. Wiley-VCH.

British Standard (BS) 1988. BS 2975 - British standard methods for sampling and analysis of glassmaking sands.

Council for Scientific and Innovative Research (CSIR). 2013. Characterizing the risk of human exposure and health impacts from acid mine drainage in South Africa - “Final Project Report”. Mine Health and Safety Council.

David, M.I. 2011. A Study of Silica sand Quality and End Uses in Surrey and Kent. Available online: http://www.Ist-glass.Istthings.com/articles/glasscolouring.html (accessed in 12 July 2011).

de Melo, V.A.R., Lameiras, F.S., Tolentino, E. 2012. Conversion of Sandy Tailing from Banded Iron Formation Exploitation into Glass-ceramic Materials. Materials Research. 15 (1), 15-20.

Department of Minerals and Energy (DME) 2004. The silica industry in the Republic of South Africa. Directorate: Mineral Economics. ISBN: 1-919927-01-8.

Department of Minerals and Energy (DME) 2017. Minerals statistical tables 1995 - 2016. Directorate: Mineral Economics. ISBN: 978-0-621-45963-0.

Duvuna, G.A., Ayuba, A. 2015. A study on silica sand quality in Yazaram and Mugulbu deposits for glass making. Nigerian Journal of Technology. 34 (1), 109 - 112.

Edem, C.A., Malu, S.P., Ita, B.I. 2014. Characterization and beneficiation of the glass making potentials of silica sand deposit from River Benue North Central Nigeria. Journal of Natural Sciences Research. 4 (19), 49 - 58.

Entwistle, J.A., Hursthouse, A.S., Marinho Reis, P.A., Stewart, A.G. 2019. Metalliferous Mine Dust: Human Health Impacts and the Potential Determinants of Disease in Mining Communities. Current Pollution Reports. 5, 67–83.

European Commission (EC) 2007. Raising Productivity Growth: Key Messages from The European Competitiveness Report, Commission of The European Communities (SEC (2007) 1444).

Fashola, M.O., Ngole-Jeme, V.M., Babalola, O.O. 2016. Heavy Metal Pollution from Gold Mines: Environmental Effects and Bacterial Strategies for Resistance. International Journal of Environmental Research and Public Health. 13 (11), 1047.

Favas, P.J.C., Sarkar, S.K., Rakshit, D., Venkatachalam, P., Prasad, M.N.V. 2016. Acid mine drainages from abandoned mines, hydrochemistry, environmental impact, resource recovery, and prevention of pollution. In Environmental Materials and Waste—Resource Recovery and Pollution Prevention; Prasad, M.N.V. and Shih, K. Eds; Elsevier: Amsterdam, Netherlands, 2016, 413–462. doi.org/10.1016/B978-0-12-803837-6.00017-2.

Garcia-Valles, M., Avila, G., Martinez, S., Terradas, R., Nogue´s, J.M. 2007. Heavy metal-rich wastes sequester in mineral phases through a glass–ceramic process. Chemosphere. 68, 1946 – 1953.

Garside, M. 2019. Glass industry - Statistics & Facts. Statista. Hamburg, Germany. 4108/glass/.

GWP Consultants. 2010. A study of silica sand quality and end uses in Surrey and Kent.

Haghi, H., Noaparast, M., Tonkaboni, S.Z.S., Mirmohammadi, M. 2016. A new experimental approach to improve the quality of low grade silica; the combination of indirect ultrasound irradiation with reverse flotation and magnetic separation. Minerals. 6, 121.

Hasanuzzaman, M., Rafferty, A., Sajjia, M., Olabi, A. 2015. Properties of glass materials, In Reference Module in Materials Science and Materials Engineering; Lauter, V., Lauter, H., Glavic, A; Elsevier: Amsterdam, Netherlands. doi,10.1016/B978-0-12-803581-8.03998-9.

Haugsten, K.E., Gustavson, B. 2000. Environmental properties of vitrified fly ash from hazardous and municipal waste incineration. Waste Management. 20, 167 – 176.

Heck, M., Hoffmann, P. 2002. Analysis of early medieval glass beads: The raw materials to produce green, orange and brown colours. Mikrochimica Acta. 139, 71 - 76.

Holand, W., Deubener, J. 2017. Nucleation and crystallization of glasses and glass-ceramics. Mauro JC, In: Frontiers in materials. Corning Inc. USA. ISSN: 1664-8714.

Hubert, M. 2015. Commercial glass compositions, properties and technical considerations – Raw materials. IMI-NFG Course on Processing in Glass. CelSian Glass & Solar Eindhoven, The Netherlands.

Kinnunen, P., Ismailov, A., Solismaa, S., Sreenivasana, H., Räisänen, M., Levänen, E., Illikainen, M. 2018. Recycling mine tailings in chemically bonded ceramics – A review. Journal of Cleaner Production. 174, 634-649.

Ko, T., Chu, C. 2018. Evaluation of Acid Leaching on the Removal of Heavy Metals and Soil Fertility in Contaminated Soil. Journal of Chemistry. Article ID 5036581.

Krewski, D., Yokel, R.A., Nieboer, E., Borchelt, D., Cohen, J., Harry, J., Kacew, S., Lindsay, J., Mahfouz, A.M., Rondeau, V. 2007. Human health risk assessment for aluminium, aluminium oxide, and aluminium hydroxide. Journal of toxicology and environmental health. Part B, Critical reviews, 10 Suppl 1(Suppl 1); 1-269.

Lockhart, B. 2006. The Color Purple: Dating Solarized Amethyst Container Glass. Historical archaeology. 40 (2), 45-56.

Malu, S.P., Edem, C.A., Ita, B.I. 2015. Chemical characterization of silica sand deposit from River Katsina-ala, North Central Region of Nigeria. Global Journal of Pure and Applied Chemistry Research. 3 (1), 26 - 40.

Momoh, A., Mhlongo, S.E., Abiodun, O., Muzerengi, C., Mudanalwo, M. 2013. Potential implications of mine dusts on human health: A case study of Mukula Mine, Limpopo Province, South Africa. Pakistan Journal of Medical Sciences. 29 (6), 1444 – 1446.

Nelson, G., Murray, J., Phillips, J.I. 2011. The Risk of Asbestos Exposure in South African Diamond Mine Workers. The Annals of Occupational Hygiene. 55 (6), 569 – 577.

Ng, J.C., Ciminelli, V., Gasparon, M., Caldeira, C. 2019. Health risk apportionment of arsenic from multiple exposure pathways in Paracatu, a gold mining town in Brazil. Science of The Total Environment. 673, 36-43.

Ngole-Jeme, V.M., Fantke, P. 2017. Ecological and human health risks associated with abandoned gold mine tailings contaminated soil. PLoS ONE. 12 (2), e0172517.

Okereafor, U., Makhatha, M., Mekuto, L., Uche-Okereafor, N., Sebola, T., Mavumengwana, V. 2020. Toxic Metal Implications on Agricultural Soils, Plants, Animals, Aquatic life and Human Health. International Journal of Environmental Research and Public Health. 17 (7), 2204.

Okereafor, G., Makhatha, M., Mekuto, L., Mavumengwana, V. 2019. Evaluation of Trace Elemental Levels as Pollution Indicators in an Abandoned Gold Mine Dump in

Ekurhuleni Area, South Africa. IntechOpen. London, UK. doi: 10.5772/intechopen.89582.

Olobatoke, R.Y., Mathuthu, M. 2016. Heavy metal concentration in soil in the tailing dam vicinity of an old gold mine in Johannesburg, South Africa. Canadian Journal of Soil Science. 96 (3), 299 – 304.

Oyewo, O.A., Agboola, O., Onyango, M.S., Popoola, P., Bobape, M.F. 2018. Current methods for the remediation of acid mine drainage including continuous removal of metals from wastewater and mine dump. In Bio-Geotechnologies for Mine Site Rehabilitation; Prasad, M.N.V., de Campos Favas, P.J. and Maiti, S.K. Eds; Elsevier: Amsterdam, Netherlands, 103–114. doi.org/10.1016/B978-0-12-812986-9.00006-3.

Pe´rez, J.A., Terradas, R., Seijas, M.M., Manent, R., Martı´nez, S. 1996. Inertization of industrial wastes in ceramics materials. Industrial Ceramic. 16, 7 - 11.

Pisutti, D., Prukswan, C., Pornsawat, W., Narin, S. 2008. Investigation of local quartz sand for application in glass industry. Advances in Geosciences. 13, 23 - 29.

Plumlee, G.S., Morman, S.A. 2011. Mine Wastes and Human Health. Elements. 7, 399–404.

Rangel, B.F., Viana, M.M., Fonseca, M.V.A., Dweck, J., Tavares, L.M. 2015. Thermal characterization of a new green ceramic material by heating microscopy, thermogravimetry and differential thermal analysis. Journal of Thermal Analysis and Calorimetry. 121, 115 – 125.

Rösner, T., van Schalkwyk, A. 2000. The environmental impact of gold mine tailings footprints in the Johannesburg region, South Africa. Bulletin of Engineering Geology and the Environment. 59, 137–148.

Singh, P., Nel, A., Durand, J.F. 2017. The use of bioassays to assess the toxicity of sediment in an acid mine drainage impacted river in Gauteng (South Africa). Water SA. 43 (4), 673 – 683.

Sundararajan, M., Ramaswamy, S., Raghavan, P. 2009. Evaluation for the beneficiability of White silica sands from the overburden of Lignite mine situated in Rajpardi district of Gujarat, India. Journal of Minerals Materials Characterization and Engineering. 8 (9), 701 - 713.

Tabelin, C.B., Igarashi, T. 2009. Mechanisms of arsenic and lead release from hydrothermally altered rock. Journal of Hazardous Materials. 169 (1-3), 980-990.

Tarasova, I.I., Dudeney, A.W.L., Pilurzu, S. 2001. Glass sand processing by oxalic acid leaching and photo catalytic effluent treatment. Minerals Engineering. 14, 639 - 646.

Tchounwou, P.B., Yedjou, C.G., Patlolla, A.K., Sutton, D.J. 2012. Heavy metal toxicity and the environment. Experientia supplementum. 101, 133–164.

Tomiyama, S., Igarashi, T., Tabelin, C.B., Tangviroon, P., Ii, H. 2019. Acid mine drainage sources and hydrogeochemistry at the Yatani mine, Yamagata, Japan: A geochemical and isotopic study. Journal of Contaminant Hydrology. 225, 103502.

Vatalis, K.I., Charalampides, G., Platias, S., Benetis, N.P. 2014. Market Developments and Industrial Innovative Applications of High Purity Quartz Refines. International Conference on Applied Economics (ICOAE) Procedia Economics and Finance. 14, 624 – 633.

Veglio, F., Passariello, B., Abbruzzese, C. 1999. Iron removal process for high-purity silica sand production by oxalic acid leaching. Industrial and Engineering Chemical Research. 38, 4443 - 4448.

Wesgro. 2018. Glass Sector Fact Sheet.

Wintour, N. 2015. WP 310 - The glass industry : recent trends and changes in working conditions and employment relations. International Labour Office, Sectoral Policies Department. - Geneva: ILO.

Ye, C., He, F., Shu, H., Qi, H., Zhang, Q., Song, P., Xie, J. 2015. Preparation and properties of sintered glass–ceramics containing Au–Cu tailing waste. Materials & Design. 86, 782-787.

CHAPTER 7

SUMMARY AND CONCLUSION

Summary and conclusion

7.1 Summary.

There are increasing interests in the mining industry and the occurrence of waste materials such as tailings (Jensen & Pedersen, 2006; Maier, *et al*. 2014; Woodward & Hales, 2014). The generation of mine tailings as reported in previous studies amongst other things is a consequence for harnessing the natural resources within the earth crust in the quest for providing raw materials for industries, boost the economy by job creation and revenue from export commodities (Lottermoser, 2007). More precisely, a need to pinpoint probable health hazards and environmental decadence that may emanate from this engineering act has begun (Abdul-Wahab & Marikar, 2012; Ngole-Jeme & Fantke, 2017). Mining in general leaves negative footprints on the environment such as water pollution, loss of biodiversity, soil erosion and pollution, and the formation of sinkholes (Chepkemoi, 2017). The ecosystem of places associated with intense mining activities is probably at risk of exposure to potentially harmful mineralogical, biological, and non-biological soil, air, and water contents. Some of the prominent challenges of mining waste exposure include the issues of acid mine drainages, reduction in agricultural land, and health hazards (Stewart, 2019). The latter deals more with potentially toxic metals poisoning as a result of interaction within the ecosystem.

From this study, it was revealed that most of the sediments were mostly dominated by fine sand and silt/clay that is highly contaminated by Cd, Cr, and Pb going by the USEPA sediment quality guidelines. Other environmental assessment indices such as pollution load index indicated that the sediments in the tailings dump are polluted while the geo-accumulation index revealed that Cr, Pb, and As contaminated the site, thus indicating very high degrees of contamination of the sediments at the mine dump (see chapter three).

It was further indicated that agricultural activities will not strive within the study area as the tailing sediments were largely comprised of fine sands that are loosely packed and prone to erosion. This could result in erosion and subsequent migration of trace metal contaminants trapped in tailing sediments into water sources, surrounding soils, and the atmosphere. Hence the high levels of Al, As, Pb, and Cr observed in the wetland and rivers around the tailings site all of which compromises sustainable agricultural activities within the surrounding farmlands. This may also have a health-related effect on the human population that resides in proximity to this mine dump (see chapter four).

The presence and survival of *Hyparrhenia hirta* within the tailings dump was a good gesture. An assessment of the levels of trace elements in both the grass specie and the tailings indicated the possibility of the former being qualified as a hyperaccumulator as it is suitable for rehabilitation of the tailings dump (see chapter five).

An aspect of this study considered the use of the silica sands from the gold mine tailings for glass production. The granulometric analysis revealed the gold mine tailings sediments to be having over 80 % silica with some level of impurities. The tailings sediments also met the international glass manufacturers' requirements in terms of physical properties such as grain size, grain morphology, and moisture content. Considering that there have been no studies or attempts at using gold mine tailings as silica sand source for industrial glassmaking, laboratory trials were conducted. This study revealed a novelty from the laboratory attempts at using the gold mine tailings with some fluxing materials to produce glass with green colouration (see chapter six).

7.2 Recommendations.

The use of multi-disciplinary, evidence-based solutions is required in dealing with environmental problems like global warming, acid rain, air pollution, urban sprawl, waste disposal, ozone layer depletion, water pollution, climate change and many more that are endlessly affecting humans, animals, and plants. It is therefore imperative to further beneficiate the gold tailings sediments to improve its usage for various glass applications. Also, the characterisation of the laboratory-produced glass should be carried out to establish the quality of glass and areas of application.

References.

Abdul-Wahab, S.A., Marikar, F.A. 2012. The environmental impact of gold mines: pollution by heavy metals. Central European Journal of Engineering, 2 (2), 304 – 313.

Chepkemoi, J. 2017. What is the environmental impact of the mining industry? World Atlas, worldatlas.com/articles/what-is-the-environmental-impact-of-the-mining-industry.html.

Jensen, J., Pedersen, M.B. 2006. Ecological risk assessment of contaminated soil. Reviews of Environmental Contamination and Toxicology, 186, 73 - 105.

Lottermoser, B. 2007. Mine Wastes: Characterization, Treatment and Environmental Impacts. Springer; New York, NY, USA. pp. 1–290.

Maier, R. M., Dı´az-Barriga, F., Field, J. A., Hopkins, J., Klein, B., & Poulton, M. M. (2014). Socially responsible mining: The relationship between mining and poverty, human health and the environment. Reviews on Environmental Health, 29, 83–89.

Ngole-Jeme, V.M., Fantke, P. 2017. Ecological and human health risks associated with abandoned gold mine tailings contaminated soil. PloS one, 12(2), e0172517.

Stewart, A.G. 2019. Mining is bad for health: a voyage of discovery. Environmental Geochemistry and Health.

Woodward, A., Hales, S. 2014. The past and future of coal. Australian and New Zealand Journal of Public Health, 38 (2), 103–104